PB-221 603

CHEMICAL AND PHYSICAL CHARACTERIZATION OF AUTOMOTIVE EXHAUST PARTICULATE MATTER IN THE ATMOSPHERE

C. W. Melton, et al

Battelle Columbus Laboratories

Prepared for:

Coordinating Research Council, Incorporated
Research Triangle Park, North Carolina

14 June 1973

DISTRIBUTED BY:

NTIS

National Technical Information Service
U. S. DEPARTMENT OF COMMERCE
5285 Port Royal Road, Springfield Va. 22151

BIBLIOGRAPHIC DATA SHEET	1. Report No. CRC-APRAC-CAPE-19-70-2	2.	3. Recipient's Accession No. PB-222 603
4. Title and Subtitle Chemical and Physical Characterization of Automotive Exhaust Particulate Matter in the Atmosphere			5. Report Date June 14, 1973 6.
7. Author(s) C.W. Melton, R.I. Mitchell, D.A. Trayser, J.F. Foster,			8. Performing Organization Rept. No.
9. Performing Organization Name and Address Battelle Columbus Laboratories 505 King Avenue Columbus, Ohio 43201			10. Project/Task/Work Unit No. CRC-APRAC CAPE-19 11. Contract/Grant No.
12. Sponsoring Organization Name and Address Coordinating Research Council, Inc., 30 Rockefeller Plaza, New York, N.Y. 10020 and the Environmental Protection Agency, Research Triangle Park, North Carolina 27711			13. Type of Report & Period Covered Final 14.

15. Supplementary Notes

Additional copies available upon request.

16. Abstracts

This report describes a third year of studies directed toward determining the fate of auto exhaust particles in the atmosphere. Experimental apparatus and procedures have been developed, and analytical data have been accumulated on particle characteristics and morphology. In the year covered by this report, preparation, instrumentation and deposit conditioning of two automobiles has been completed in preparation for systematic examination of particulate emissions during the coming year. Environmental variables are to be studied for influences on the properties and fate of aerosols emitted by the automobiles and diluted by mixing with the ambient atmosphere. This report is presented in two major sections describing first the experimental apparatus and procedures, and then the experimental results with discussion of their significance and interpretation.

17. Key Words and Document Analysis. 17a. Descriptors

Air Pollution
Exhaust Gas
Particulates
Fuels
Velocity
Aerosol
Emissions
Morphology

17b. Identifiers/Open-Ended Terms

17c. COSATI Field/Group 13B; 21B; 21D; 11D; 6-C.

18. Availability Statement	19. Security Class (This Report)	21. No. of Pages
Releasable to the public.	UNCLASSIFIED	90
	20. Security Class (This Page) UNCLASSIFIED	22. Price #3.00/#0.95

FORM NTIS-35 (REV. 3-72) THIS FORM MAY BE REPRODUCED USCOMM-DC 14952-P72

PB 221 603

FINAL SUMMARY REPORT

on

CHEMICAL AND PHYSICAL CHARACTERIZATION OF AUTOMOTIVE EXHAUST PARTICULATE MATTER IN THE ATMOSPHERE

to

COORDINATING RESEARCH COUNCIL
(CRC-APRAC PROJECT NO. CAPE-19-70)

and

ENVIRONMENTAL PROTECTION AGENCY
(CONTRACT NO. 68-02-0205)

June 14, 1973

Period Covered: June 25, 1971, to June 30, 1972

by

C. W. Melton, R. I. Mitchell, D. A. Trayser
J. F. Foster, Project Director

Reproduced by
NATIONAL TECHNICAL
INFORMATION SERVICE
U S Department of Commerce
Springfield VA 22151

BATTELLE
Columbus Laboratories
505 King Avenue
Columbus, Ohio 43201

Battelle is not engaged in research for advertising, sales promotion, or publicity purposes, and this report may not be reproduced in full or in part for such purposes.

Battelle
Columbus Laboratories
505 King Avenue
Columbus, Ohio 43201
Telephone (614) 299-3151
Telex 24-5454

June 14, 1973

Mr. A. E. Zengel
Project Manager
Coordinating Research Council
30 Rockefeller Plaza
New York, New York 10020

Dear Mr. Zengel:

Enclosed are 300 copies of the Summary Report on "Chemical and Physical Characterization of Automotive Particulate Matter in the Atmosphere" for the contract year July 1, 1971, to June 30, 1972. The report has been approved in this revision by the APRAC/CAPE-19-70 Project Group.

Yours very truly,

John F. Foster

John F. Foster, Project Director
Emissions Control and Environmental Systems

JFF/md

Enclosures (300)

cc: Mr. R. F. Bauer
Mr. C. R. Begeman
Mr. T. C. Belian
Dr. D. S. Gray
Mr. F. P. Hochgesang
Dr. K. Habibi
Mr. M. P. Huneycutt
Dr. E. S. Jacobs
Dr. J. B. Moran
Dr. G. S. Musser
Dr. W. R. Pierson
Dr. J. Wagman
Dr. W. E. Wilson, Jr.

TABLE OF CONTENTS

	Page
SUMMARY	1
INTRODUCTION	4
OBJECTIVE	5
EXPERIMENTAL APPARATUS AND PROCEDURES	5
Project Vehicles	5
Conditioning Procedures	6
Summary of Conditioning Operations	6
Details of Conditioning Operation of the Project Cars	8
Test Cycle	8
Dilution Ratios	9
Exhaust Gas Monitoring	10
Particulate Sampling From the Dilution Tunnel	10
Fuels	11
Comparison of Vehicles for Similarity	15
Standardized Operating Procedures	15
Particulate Sampling and Comparison Procedures	15
Procedures After the Transition to Different Fuels	16
Initial Tune-Up and Servicing	16
New Baseline Data	17
Collection of Particulates	19
Completion of Conditioning With Unleaded and Leaded Fuels	19
Dilution Tunnel	19
Construction and Assembly	20
Velocity and Gas Mixing Profiles	22
Aerosol Mixing Profiles	22
Modification of the Dilution Tunnel	30
Positive Pressure Operation	30
Change in Dilution Ratio	30
Aerosol Mixing Profile	30
Residence Chamber	31
Apparatus for Aerosol Monitoring	37
Filters and Impactors	37
Single Particle Counter	38

TABLE OF CONTENTS (Continued)

	Page
EXPERIMENTAL RESULTS AND DISCUSSION	42
Comparative Measurements of Vehicles	42
Gaseous Emissions From Steady-State Operation	42
Gaseous Emissions From LA-4 Cycles	46
Inorganic Composition of Exhaust Particulates	49
Morphology of Exhaust Particles	49
Organic Analysis of Exhaust Emissions by HPLC and GC	49
Exhaust Particle Sizes	55
Total Particulate Mass Loadings	55
Factors Affecting Light Scattering in the Tunnel	61
Preliminary Residence Chamber Measurements	69
Test Conditions	69
Aerosol Concentrations	71
Particle Count	71
Particle Mass	73
Particle Morphology	75
MAJOR ACCOMPLISHMENTS	77
Standardization of Test Autos	77
Construction and Operation of Test Facility	78
Conditioning of Cars	79
Preliminary Particulate Measurements	79
FUTURE WORK	82

LIST OF TABLES

Table 1.	Characteristics of Fuels	12
Table 2.	Determination of Aerosol Concentration Profiles in the Dilution Tunnel at 560 FPM	26
Table 3.	Distribution of Dye Aerosol at Replicate Sampling Sites	32
Table 4.	Exhaust Gas Composition from the Exhaust Pipe at 50-MPH Steady Cruise During Conditioning of White Car (Unleaded Fuel)	44

LIST OF TABLES (Continued)

Page

Table 5. Exhaust Gas Composition From the Exhaust Pipe at 50-MPH Steady Cruise During Break-in of Blue Car (Unleaded Fuel). 45

Table 6. Compositions of Integrated Exhaust Samples From Single Modified LA-4 Cycles 48

Table 7. Comparison of Inorganic Compositions of Particles Collected From the Dilution Tunnel 50

Table 8. Summary of Major Peaks for Five HPLC Chromatograms of Extracts From Particulates. 54

Table 9. Combined Weights of Auto Exhaust Particulates From Unleaded Fuels From Four Modified Cold-Start LA-4 Cycles on "Metricel-DM" Filters and on the Cascade Impactor and Backup Filter 58

Table 10. Weight of Auto Exhaust Particulates Collected on Metricel-DM Filters of Different Sizes and on Cascade Impactor 60

LIST OF FIGURES

Figure 1. Conditioning of Project Cars in Preparation for Testing 7

Figure 2. Air-Fuel Ratio Versus Air Flow. 18

Figure 3. Original Layout of Dilution Tunnel, With Induced Draft Blower. 21

Figure 4. Velocity and Mixing Profiles at Sampling Station 6. . . . 23

Figure 5. Sampling Probe Assembly Used for Aerosol Mixing Studies in the Dilution Tunnel. 25

Figure 6. Dilution Tunnel Mixing Profiles for Aerosols 0.87 Micron in Diameter. 27

Figure 7. Dilution Tunnel Mixing Profiles for Aerosols 2.0 Microns in Diameter 28

LIST OF FIGURES (Continued)

Page

Figure 8. Dilution Tunnel Mixing Profiles for Aerosols 5.9 Microns in Diameter 29

Figure 9. Number Code for Sampling Port Locations, Looking Toward Automobile. 33

Figure 10a. Modified Test Apparatus with Positive Pressure Sampling 34

Figure 10b. Modified Layout of Test Apparatus with Positive Pressure Sampling 35

Figure 10c. Layout of Residence Chamber and Purge-Circulation System 36

Figure 11. Photograph of Single-Particle Counter. 40

Figure 12. Calibration of Single Particle Counter with Signal Generator. 41

Figure 13. Calibration of Single Particle Counter with Polystyrene Latices 43

Figure 14. HC Concentrations Sampled From the Exhaust at 50 MPH Steady Cruise During Break-in of Project Cars . . 47

Figure 15. Typical Carbon-Black-Type Exhaust Particles From Unleaded Fuel Collected From the Tunnel on 0.25 μm Stage of Impactor. 51

Figure 16. Typical Tar-Droplet-Type Exhaust Particles From Unleaded Fuel Collected From the Tunnel on 0.5 μm Stage of Impactor. 51

Figure 17. Particle Size Distribution in Auto Exhaust Generated by the White Car with Unleaded Gasoline RE-141B. 56

Figure 18. Particle Size Distribution in Auto Exhaust Generated by the Blue Car with Unleaded Gasoline RE-141B 57

Figure 19. Particle Size Distribution in Automobile Exhaust Generated by the White Car with Unleaded Gasoline at 50 MPH Steady State 62

Figure 20. Particle Size Distribution in Automobile Exhaust Generated by the Blue Car with Leaded Gasoline at 50 MPH Steady State. 63

LIST OF FIGURES (Continued)

Page

Figure 21. Typical Light-Scattering Patterns for Different Initial Temperature Conditions, Blue Car 65

Figure 22. Correlation Between Light-Scattering and Initial Choke-Box Temperature, Blue Car. 67

Figure 23. Light-Scattering Patterns for Consecutive Partial Modified LA-4 Cycles Using Controlled-Choke Schedule 1 - Blue Car. 68

Figure 24. Light-Scattering Patterns for Consecutive Partial Modified LA-4 Cycles Using Controlled-Choke Schedule 2 - Blue Car. 70

Figure 25. Particles in Residence Chamber, Run 4 72

Figure 26. Particle Size Distribution of Diluted Automobile Exhaust in Chamber (Run 4) 74

Figure 27. Particles Collected on the 1/4 μm Impactor Stage After Six Hours in the Residence Chamber 76

Figure 28. A Particle Typical of Those Collected on the 1.0- m Impactor Stage After Six Hours Residence Time. 76

CHEMICAL AND PHYSICAL CHARACTERIZATION OF AUTOMOTIVE EXHAUST PARTICULATE MATTER IN THE ATMOSPHERE

By

C. W. Melton, R. I. Mitchell, D. A. Trayser
J. F. Foster, Project Director

SUMMARY

Two matched autos have been made operative to generate exhaust particulate matter. These 1970 Fords are equipped with measured and matched 1971 351 CID engines, automatic transmissions, and 2-barrel carburetors. These cars were chosen to represent a typical and large volume sales car model. To achieve reproducible operation of the cars for generating the exhaust particles, a chassis dynamometer with an automatic driver programmed for the 1972 FTP driving schedule is used. Forced-air cooling of the exhaust system is used during the tests to maintain operating temperatures similar to measured values during operation on the highway.

A typical unleaded fuel was purchased in sufficient quantity to supply the projected needs of the project. A portion of this fuel was then leaded with TEL motor mix to 2.49 g/gallon lead. Thus both fuels have identical compositions except for the added TEL motor mix.

Initially, each car was driven for 4000 miles with unleaded fuel on a (modified) Durability Driving Schedule. Periodic tests during this stabilization period established their matched condition. Stabilization was completed after operation for another 4000 miles on the Durability Driving Schedule with unleaded fuel in one car and leaded fuel in the other. An exhaust gas dilution tunnel has been built and calibrated. The diluted exhaust passes through a measuring and mixing orifice and along the length of the 36-foot stainless steel tunnel which has a 23-inch diameter. Typically,

the exhaust is diluted an average of 20:1 or 30:1 by appropriate control of the tunnel air flow.

Exhaust gas composition is monitored continuously for CO, HC, CO_2, and NO in the tunnel and a CVS type bag sample is also taken in order to appraise reproducibility of vehicle operation.

A 2100 cu. ft. residence chamber has been constructed for collection of a proportional sample of the tunnel flow. Final dilution is about 300:1 in order to minimize wall effects and be more representative of atmospheric dilution. Walls of the chamber are flexible opaque film mounted on a collapsible frame to minimize photochemical interactions, and to maintain negligible pressure difference between sample and surroundings while the chamber is in use to collect, store, and then withdraw samples. Temperature, humidity, gaseous composition, and particle content in the chamber are monitored over a range of residence times. Particles are collected simultaneously for detailed analysis.

Measurements of the mass of particulate emissions collected on Metricel-DM membrane filters showed variations in the collected amounts with the face velocity of the exhaust as well as with the operating cycle and fuel used.

Particle-size distributions were measured in the Battelle impactor, which collects fractions on six impact stages with cut-offs at sizes ranging from 8 to 0.25 micrometers mass mean equivalent diameter. An absolute filter is used to back up the last stage of the impactor.

The properties of the aerosol particles in diluted exhaust were examined in exploratory measurements while the aerosol was aged in the residence chamber. The overall results in these preliminary studies suggest

that the smallest particles below the light-scattering range agglomerate or grow during the first two hours to a size sufficient to scatter light. Thereafter light-scattering measurements indicate little change in the aerosol. Other measurements, by a single-particle counter, also indicate growth and agglomeration. Some particle growth appears to continue as long as 24 hours, accompanied by precipitation of the largest particles.

Samples were withdrawn from the chamber after six hours residence and passed through 142-mm and 47-mm filters, and an impactor with back-up 76-mm filter. The weight gains recorded after filtration of identical volumes of gas in concurrent samples (60 minutes at 1 cfm) varied widely and correlated qualitatively with the diameters or areas of filters used. No conclusions were possible concerning the absolute weight concentration of the filterable aerosol particles.

The studies on characterization of auto exhaust particles are being continued. The changes attributable to leaded vs. unleaded fuel, residence time, relative humidity, and the concentrations of two common atmospheric pollutants are to be studied in a series of tests designed to show statistically significant differences in particle properties. The variability of weights of particles collected on filters resulting from variations in filter properties and in collection conditions represents a serious handicap in the search for quantitative interpretations of the characteristics of exhaust particulate matter in the atmosphere. Studies will be continued with comparison of results on a relative scale, and efforts to resolve the problem of measuring the absolute mass concentration of auto exhaust particulates will be continued.

INTRODUCTION

This report describes a third year[1,2] of studies directed toward determining the fate of auto exhaust particles in the atmosphere. Experimental apparatus and procedures have been developed, and analytical data have been accumulated on particle characteristics and morphology. In the year covered by this report, preparation, instrumentation and deposit conditioning of two automobiles has been completed in preparation for systematic examination of particulate emissions during the coming year. Environmental variables are to be studied for influences on the properties and fate of aerosols emitted by the automobiles and diluted by mixing with the ambient atmosphere.

This report is presented in two major sections describing first the experimental apparatus and procedures, and then the experimental results with discussion of their significance and interpretation. Some of the information on apparatus, equipment and operations in the preceding annual report is repeated in order that this summary report shall be comprehensible without major dependence on preceding annual reports.

---

(1) C. W. Melton, et al., "Physical-Chemical Characteristics of Particles Associated with Polynuclear Aromatic Hydrocarbons Present in Automobile Exhaust", Final Summary Technical Report for the period January 24, 1969, to March 31, 1970, to Coordinating Research Council (APRAC-CAPE-12-68-Neg. 59), January 29, 1970.

(2) J. F. Foster, et al., "Chemical and Physical Characterization of Automotive Exhaust Particulate Matter in the Atmosphere", Final Summary Report for the period July 1, 1970, to June 24, 1971, to Coordinating Research Council (CAPE-12-68-Neg. 59 and CAPE—19-70) October 6, 1972.

OBJECTIVE

The objective of the CAPE-19 project is to characterize exhaust particulates generated under "real-life" conditions from both leaded and unleaded gasolines, with the long-range goal being the definition of the fate of automobile-generated particulates in the atmosphere. Along this line, attempts will be made analytically to characterize organic-inorganic associations which exist in automobile exhaust particles generated under various conditions and after having interacted with prevalent extraneous nuclei such as silica (SiO_2).

EXPERIMENTAL APPARATUS AND PROCEDURES

Project Vehicles

Two 1970 Fairlane Fords with matched 1971 engines were prepared for exhaust-gas generation; one was run with unleaded fuel and the other with leaded fuel. Each vehicle was equipped with a 351 CID V-8 engine, 2-barrel carburetor, and automatic transmission. In order to make the two automobiles as nearly comparable as possible, specially matched and measured 1971 engines were made available by the Ford Motor Company and were installed in the two vehicles by project personnel at Battelle.

To identify each car in this report, one of them will be referred to as the white car; only unleaded fuel was used in its operation. The other will be referred to as the blue car; only leaded fuel was used in its operation after completion of deposit conditioning runs and collection of base-line data on unleaded fuel.

Both vehicles were checked after delivery for driveability and mechanical condition, and were found to be satisfactory. The checkout included both visual examination and city-street and highway driving. Preliminary studies of exhaust particulate collection and development of procedures were conducted with the white (unleaded car) to gain experience with operating the vehicle in a test mode, before installation of the 1971 measured engine. Both vehicles were provided with instrumentation for monitoring performance, as discussed in the preceding Final Summary Report for 1970-1971. Vehicle history and further modification during the current year are described on the following pages.

Conditioning Procedures

Summary of Conditioning Operations

Figure 1 summarizes the conditioning operations. Both the blue and white cars were conditioned for deposits using a modified Durability Driving Schedule for a total of 4000 miles, and using unleaded Fuel No. RE141A. During the conditioning period, comparisons were made of automobile operating parameters, and exhaust emissions in samples of diluted exhaust taken from a dilution tunnel, to appraise the comparability of the two cars. Later, new fuels, one leaded and the other unleaded, were obtained and the conditioning was repeated. First, both cars were run 200 miles on the new unleaded fuel, RE-141B, to determine how the vehicles operating with the new fuel compared to one another. Then the blue leaded car was switched to the new leaded fuel, RE-141C, and 4000 additional miles were accumulated while running according to the Durability Driving Schedule. The white unleaded

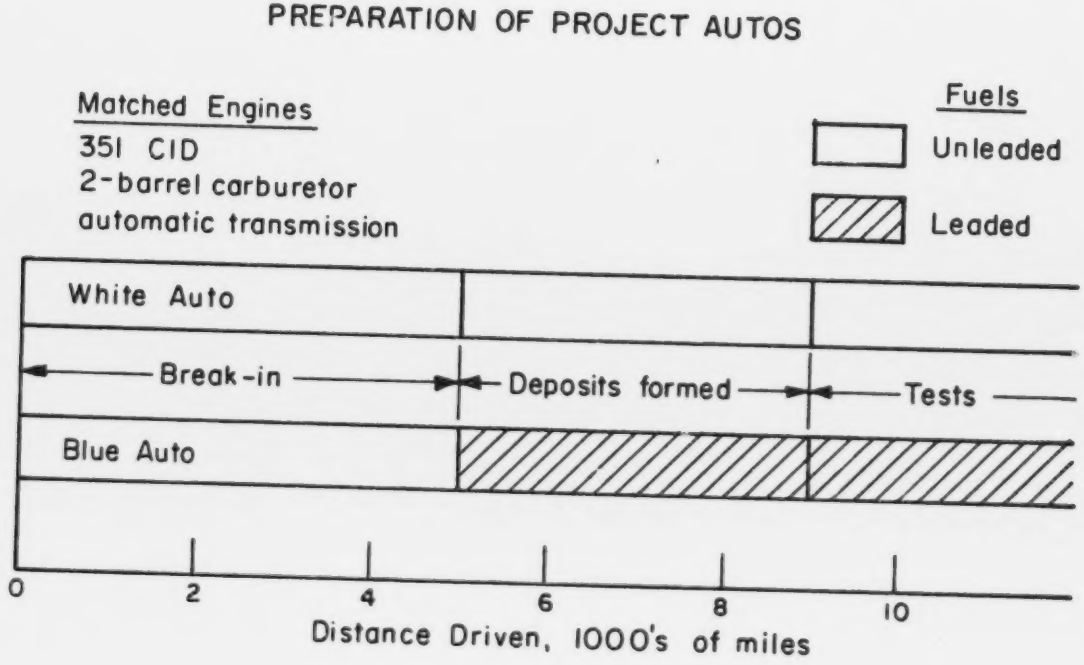


FIGURE 1. CONDITIONING OF PROJECT CARS IN PREPARATION FOR TESTING

car was run again with the new unleaded gasoline RE-141B to accumulate the same mileage as the blue leaded car. At this point, the cars were considered adequately conditioned and ready for generation of exhaust particulate for residence chamber experiments.

Details of Conditioning Operation of the Project Cars

The initial operation of each project car for 4000 miles used part of the proposed Durability Driving Schedule, given in the July 15, 1970, Federal Register. The 70-mph lap was not used. The initial conditioning runs for deposit stabilization used unleaded fuel in both cars. The 4000 miles were logged in two months with the white car and in two weeks with the blue car.

The ignition timing, points dwell, points gap, and idle speed were checked on each car at the beginning and at the end of the conditioning period. Also, the condition of the spark plugs and ignition points were checked at the end. No significant wear or deterioration was observed. After 4000 miles, the ignition timing of the white (unleaded) car was found to be retarded about 5 degrees from manufacturer's specification. Timing was reset and a test run made to determine if the change had any effect on exhaust emissions. No change in HC or CO in the exhaust was observed.

Test Cycle

One test cycle was selected and used in all studies described here to generate particles from each of the two cars. The selected cycle was based on the 1972 Urban Driving Schedule with modified vehicle preconditioning

and starting procedures. Instead of the overnight cold soak called for in the Federal Test Procedure (FTP), a rapid cooldown procedure was used. The car was operated through a full cycle to establish uniform operating temperatures, then cooled rapidly by using a heat exchanger for the engine coolant and blowers for the exhaust system, radiator, and choke box. Cooldown was continued until all temperatures except the oil sump were 80 F or lower. A thermocouple was installed in the choke box to permit monitoring air temperature at the thermostatic spring during each cold-start modified LA-4 cycle. Approximately 20 minutes were required for the rapid cooldown to lower the temperatures to 80 F.

After rapid cooldown, the car was started and run through the test cycle. The starting procedure was modified from the standard FTP by adding 20 seconds to the initial idle period right after engine start to minimize the chance of engine stumble or stall.

Dilution Ratios

Tests with the project cars are described throughout this report in which the progress of conditioning or the characteristics of gaseous and particulate emissions were measured. When a dilution tunnel was used, the dilution ratios given as part of the data were derived from the following measured parameters. These values are valid except when otherwise stated for specific tests.

In general, the dynamometer load was 6 HP during conditioning procedures. Thereafter, the test fuel was changed in January, 1972, from RE-141A (unleaded) to either RE-141B (unleaded) or RE-141C (leaded), and the dynamometer load was increased to 12 HP.

Car Operation	Modified LA-4 Cycle	Modified LA-4 Cycle	50 MPH Steady State	50 MPH Steady State
Dynamometer Load, hp (Set at 50 mph)	6	12	6	12
Exhaust Gas Flow, scfm (average)	25	30	46	54
Tunnel Gas Flow, scfm	600	600	1,500	1,500
Dilution Ratio	24	20	33(32.6)	28(27.8)

Exhaust Gas Monitoring

At intervals during the conditioning of the project cars, the hydrocarbon (HC) and carbon monoxide (CO) concentrations in the exhaust gases were measured while the vehicle operated at 50-mph steady-state cruise. Exhaust-gas data (shown in Tables 4 and 5, pages 44 and 45) are for a fully warmed up engine. HC was measured with a Beckman 109A Nondispersive Infrared Analyzer, and CO was measured with an Olson-Horiba MEXA-200 Nondispersive Infrared Analyzer. Exhaust-gas sampling was done with a 1/8-inch stainless steel probe located in an exhaust-gas diverter valve. Before entering the analyzers, the sample gas passed through an ice-bath cold trap and a glass fiber filter to remove water vapor and particulates.

Particulate Sampling From the Dilution Tunnel

Particulate sampling runs with the dilution tunnel were made at the beginning of the conditioning schedule for each car and at approximately 1000-mile intervals thereafter. These runs were made with the car operating at 50-mph steady cruise, and with a dilution tunnel air flow of 1500 scfm

(for a dilution ratio of about 33 to 1). All runs were made with a fully warmed up engine and exhaust system, and all sampling was done at the 35-foot sampling station (Station 6, Figure 3, page 21) in the tunnel.

Total particulate samples were collected for one hour on 47-mm diameter silver membrane and cellulose ester membrane filters (0.45 μm and 0.80 μm nominal pore diameter, respectively), using a sampling flow rate of 1 scfm. Particle size fractions were collected for 1/2 hour using the Battelle cascade impactor at a sampling flow rate of 1/2 scfm.

Fuels

Two different fuels, RE-141A and RE-143A, were purchased from Mobil Research and Development Corporation in July, 1971. These fuels were unleaded and leaded gasolines respectively and their organic compositions had been adjusted in order to create two fuels having very similar octane numbers. Initial conditioning of the two vehicles was accomplished with unleaded fuel RE-141A. The CAPE-19 Project Group later decided that comparisons should be made between unleaded and leaded fuels of the same organic composition, and that the octane number need not be the same. Consequently, another pair of fuels, RE-141B and 141C, were purchased from Mobil Research and Development Corporation in January, 1972. These gasolines were reported to have the same organic constituents, and differed only by the addition of TEL Motor Mix (2.49 g Pb/gal) in fuel RE-141C. The composition of RE-141A, -B, and -C are given in Table 1. Leaded fuel RE-143A was never used.

TABLE 1. CHARACTERISTICS OF FUELS

(Data supplied by Mobil Research and Development Corporation on Inspection Tests and Elemental Analyses of Gasolines Shipped to Battelle Memorial Institute in July, 1971, and January, 1972)

				Nonleaded Break-In Fuel
Blend Designation		RE-141B Battelle '72	RE-141C Battelle '72	RE-141A Battelle '71
Name		Nonleaded	Leaded	CRC White
Research Octane No. (RON)		93.6	100.0	94.0
Motor Octane No. (MON)		85.4	91.7	85.3
Vapor Pressure, Reid, Micro (D-2551)		9.0	10.6	9.6
TEL as Lead, ppm (M-1059)		0.7	-	1.2
TEL as grams Pb/gal. (M-951)		(0.002)	2.49	(0.003)
Sulfur, % wt.		0.036	-	0.020
Chlorine, ppm (M-600)		1.1	Present	1.4
Phosphorus, ppm (M-798)		<1.	1.	1.
Nitrogen, ppm (M-1042, Col.)		21	21	Not Sought
API Gravity (D-287)		60.8	60.3	Not Sought
ASTM Distillation (D-86)				
Initial Boiling Pt., °F	-16*	93	92	-
5% Distilled	63*	118	116	-
10% "	77*	132	130	125
20% "	142*	156	154	-
30% "	188*	182	178	-
40% "	207*	207	202	-
50% "	231*	228	223	218
60% "	241*	244	240	-
70% "	275*	260	256	-
80% "	292*	286	284	-
90% "	335*	331	330	324
95% "	369*	366	374	-
End Point	?*	400	403	-

* Simulated distillation by gas chromatography of RE-141B (SIMDIST ASTM Method D-2887).

TABLE 1. (Continued)

(Gas Chromatographic Analysis C_5 and Lighter;
Mass Spec HC Type Analysis C_6 and Heavier;
Chromatographic-UV Analysis BaP and BaA.
Gasolines Shipped to Battelle Memorial Institute
in July, 1971, and January, 1972)

(All results in liquid volume percent based
on total sample)

Blend Designation	RE-141B	RE-141C	Nonleaded Break-In Fuel RE-141A
Name	Battelle '72 Nonleaded	Battelle '72 Leaded	Battelle '71 CRC White
Components:			
Propylene	0.01	0.01	0.01
Propane	0.08	0.07	0.07
Isobutane	0.70	0.69	1.04
Isobutylene + Butene-1	0.07	0.06	0.18
n-Butane	5.00	5.02	4.31
trans-Butene-2	0.07	0.07	0.35
cis-Butene-2	0.09	0.09	0.35
3-Methylbutene-1	0.06	0.06	0.08
Isopentane	10.88	10.99	9.13
Pentene-1	0.16	0.16	0.32
2-Methylbutene-1	0.34	0.34	0.52
n-Pentane	2.56	2.59	2.71
trans-Pentene-2	0.41	0.42	0.62
cis-Pentene-2	0.22	0.23	0.39
Total C_5 & Lighter	(20.7)	(20.8)	(20.1)
C_6 & Heavier, Mass Spec PONA			
Paraffins	43.8	43.6	42.6
Monoolefins	3.9	4.0	4.5
Cycloolefins & Diolefins	0.6	0.6	0.8
Monocycloparaffins	1.6	1.8	2.6
Dicycloparaffins	0.2	0.2	0.2
Alkylbenzenes	27.5	27.2	27.8
Alkylindanes & -tetralins	0.8	0.9	0.8
Alkylnaphthalenes	0.8	0.9	0.6
Total C_6 & Heavier	(79.3)	(79.2)	(79.9)
Approximate Distribution of Alkylbenzenes by Mass Spec			
C_6	1.8	1.7	1.9
C_7	6.9	6.5	6.6
C_8	9.0	9.1	9.6
C_9	6.8	6.8	7.0
C_{10}	2.2	2.2	2.1
C_{11}	0.8	0.8	0.6
C_{12}	0.1	0.1	0.
Total Alkylbenzenes	(27.6)	(27.2)	(27.8)

TABLE 1. (Continued)

Blend Designation	RE-141B	RE-141C	Nonleaded Break-In Fuel RE-141A
Name	Battelle '72 Nonleaded	Battelle '72 Leaded	Battelle '71 CRC White
Total Sample GC + MS PONA Summary			
Paraffins	63.1	63.0	59.9
Olefins	5.9	6.0	8.1
Naphthenes	1.8	2.0	2.8
Aromatics	29.2	29.0	29.2
Grand Total CG & MS	100.0	100.0	100.0
Distillation-Chromatographic-UV Analysis			
Benz(a)anthracene	3.3 ppm	Not	Not
Benso(a)pyrene	1.0 ppm	Sought	Sought

Footnotes:

RE-141B and RE-141C were prepared from a single 6000 gallon lot which was composed of five blending components. These were similar to, but not exactly the same, as those in RE-141A. Those components which tend to be unstable in long term storage had antioxidant and metal deactivator additives (grades approved for use in military gasoline) added as they were produced at the refinery.

Half of the 6000 gallon lot was put into clean drums and labeled RE-141B. The other half had Tetraethyllead Motor Mix added and, after mixing, was drummed, then labeled RE-141C. TEL Motor Mix contains ethylene dichloride (1.0 theory) and ethylene dibromide (0.5 theory) according to the usual specifications. No other additives were added during blending of either RE-141B or -C. BaA and BaP in Re-141C should be the same as that determined by analysis of RE-141B. These polynuclear aromatics were not determined in RE-141A.

Comparison of Vehicles for Similarity

Standardized Operating Procedures

The project cars after break-in (see Figure 1) were run under two conditions to generate exhaust for comparison by analytical methods. One condition was the modified LA-4 cycle and the other was a 50-mph steady cruise mode.

A cold-start for the modified LA-4 cycle was achieved by use of the rapid-cooldown technique developed for the break-in operation and already described. This procedure was developed to insure that engine and exhaust system temperatures at the beginning of each modified LA-4 cycle run were consistent.

Particulate Sampling and Comparison Procedures

Particulate sampling runs were also made after break-in was completed, using the dilution tunnel and operating the car through the modified LA-4 cycle. A dilution tunnel air flow of 600 scfm was used to give an approximate 24 to 1 dilution ratio, and the driving cycle was driven from a cold (ambient temperature) start. Filters for total samples, the cascade impactor for size classification of samples, and sampling flow rates through filters and the cascade impactor were the same as for the 50-mph steady cruise dilution tunnel runs (see pages 10 and 11). One cold-start driving cycle provided sufficient samples for characterization.

Light scattering measurements were made on the diluted exhaust-gas with an integrating nephelometer during selected tunnel runs. No measurable change from filtered-air alone was observed during the 50-mph steady cruise runs. Only slight momentary increases in light scattering were observed at the beginning of the cold-start driving cycle operation.

Mainly gross analytical data were employed in organic analytical comparisons. High-pressure liquid chromatograms and gas chromatograms were used as empirical "fingerprints" of the exhaust composition, with no attempt to identify and compare specific organic compounds.

In summary, the basis for comparison of the two project cars for similarity were measurements of HC and CO in the raw exhaust, measurement of light scattering in the tunnel, particle morphology, inorganic and organic composition of collected particulate samples, and measurements of particulate mass emissions. The cars were judged to be acceptably similar.

Procedures After the Transition to Different Fuels

Initial Tune-Up and Servicing

When another set of two comparable fuels, RE-141B and -141C, was specified for use in the experimental studies, both project cars were serviced and then each was operated with the new unleaded fuel (RE-141B) for approximately 200 miles on the modified Durability Driving Schedule used in the 4000-mile conditioning operation (refer to page 8). The servicing consisted of changing the oil and oil filter, inspecting the spark plugs and points, and tuning to manufacturer's specifications.

In the servicing, it was found that two of the spark plugs and one spark plug cable of the blue car were deteriorated to the point of causing erratic operation. It is possible that this condition existed to some degree during previous particulate sampling runs, and resulted in abnormal black soot deposits noted occasionally on collection filters. No other problems were noted with either car.

The 200-mile durability operation was conducted to condition the engines and exhaust systems to the new fuel before making additional runs.

New Baseline Data

Before switching the blue car to leaded fuel, and then accumulating additional mileage on both cars, a number of different tests were made on each car to establish and compare baseline operating characteristics with the RE-141B fuel. These were (1) continuous HC and CO measurements during modified LA-4 cycles, (2) fuel consumption, (3) HC, CO and NO concentrations from modified LA-4 cycle composite bag samples, and (4) air-fuel ratios at various operating conditions.

The HC and CO concentrations obtained continuously during modified LA-4 cycles from the two cars were acceptably similar although the values for the blue car were somewhat higher than for the white car. However, variations among runs with the same car tended to be nearly as great as the differences between the two cars.

Fuel consumption was compared on the blue car between two modified LA-4 cycles, one with a hot start and the other with a cold start. The hot-start fuel consumption was 3.65 and the cold-start fuel consumption was 4.25 lb.

Air and fuel consumption were measured on both cars at warmed up steady-state conditions over the speed range using a Meriam Laminar Flow Element to determine air flow and a Kent-Moore volume type Gas-per-Mile gauge to measure gas flow. From these measurements, the relative air-fuel ratios were estimated. Figure 2 shows a plot of computed air-fuel ratio as a function of air flow, in which the cars appear to be similar with regard to carburetion.

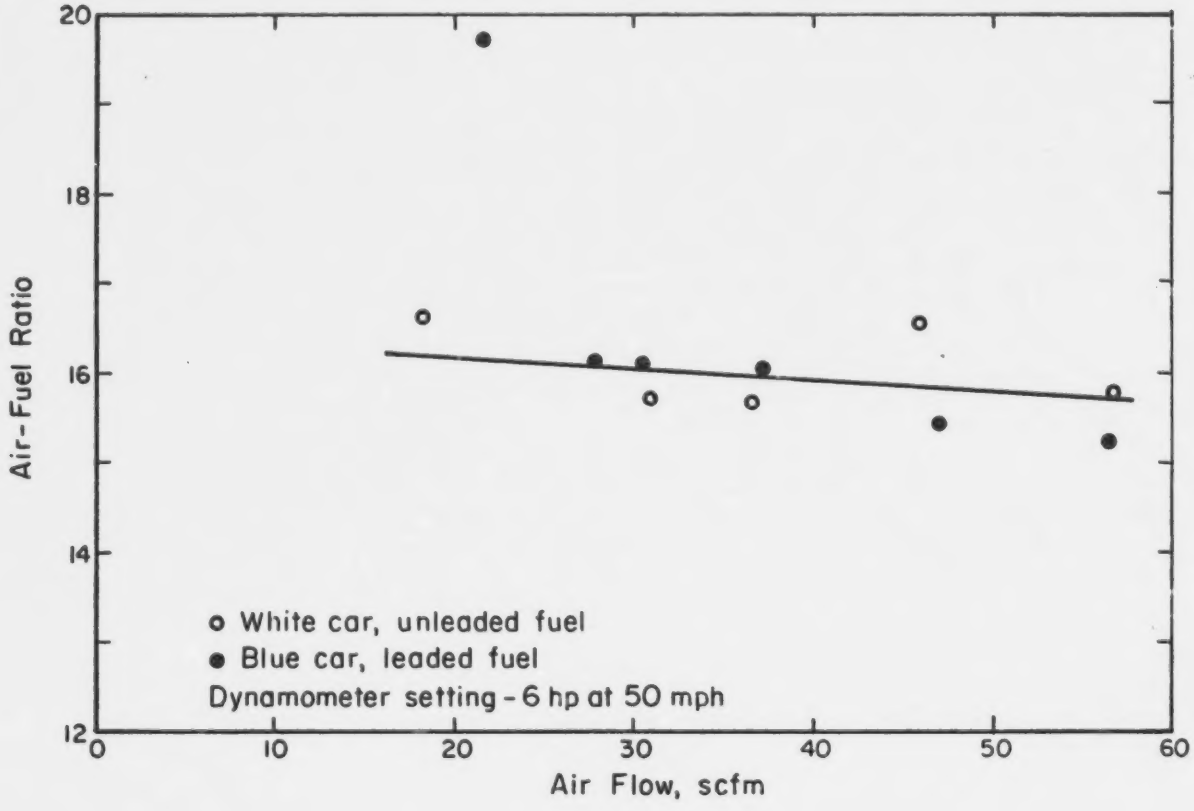


FIGURE 2. AIR-FUEL RATIO VERSUS AIR FLOW

Collection of Particulates

Particulates were collected from the new RE-141B fuel for characterization according to morphology, total mass, size distribution, and organic analysis, while the cars were operated on modified cold-start LA-4 cycles. A consistent operating procedure was followed for each cycle. The results of these runs are described on pages 47-58.

Completion of Conditioning With Unleaded and Leaded Fuels

The white (unleaded) car and the blue (leaded) car completed an additional 4000 miles conditioning on the new fuels using the modified Durability Driving Schedule. HC and CO concentrations at 50-mph steady cruise were measured periodically. At approximately 1000-mile intervals, particulate samples were collected to determine size distribution and total mass. For the particulate sampling runs, the cars were run at 50-mph steady cruise for 4 hours. The tunnel air flow was set at 400 cfm to increase the particulate concentration by decreasing the dilution ratio to about 7.4:1.

Dilution Tunnel

Exhaust gases and particulates issuing from an automobile tailpipe during over-the-road operation are rapidly quenched and diluted by the ambient atmosphere in the highly turbulent airstream near the rear of the vehicle. To simulate the real environment under reproducible experimental conditions and to permit accurate sampling of automobile exhaust, the dilution tunnel was constructed to use the technique developed by Habibi at the Du Pont Petroleum Laboratory(1).

---

(1) Habibi, Kamran, "Characterization of Particulate Lead in Vehicle Exhaust-Experimental Techniques", Environmental Science and Technology, Vol. 4, No. 3, March 1970, pp 239-253.

The design, construction, and initial negative pressure operation of the auto exhaust dilution tunnel were described in detail in the 1971 final report to CRC, but are summarized here to obviate reference to that report. During this report period, the tunnel was modified for positive pressure operation as also described in this section.

Construction and Assembly

The exhaust-gas dilution tunnel is 36 feet long by 23 inches diameter, similar to the Du Pont tunnel. Each 6-foot section was formed from a 6' x 6' sheet of 16-gage stainless steel by rolling it into a cylinder and welding the longitudinal seam. Mild steel flanges 1-1/4 inches wide were welded to each end of the tunnel sections for bolting them together.

Figure 3 is a schematic plan view of the dilution tunnel as originally assembled with blower at the downstream end, which gave negative pressures at the sampling stations. This view gives sampling station locations and the tunnel-section numbering system, which were unchanged when the tunnel was later modified for positive pressures. At each sampling station, a 1/4-inch pipe coupling was attached to the tunnel surface at the top and another on the side 90 degrees from the top. Probes were inserted through these fittings for velocity and gas concentration measurements during check-out of the tunnel. These fittings are also available for gas sampling during vehicle operation. To accommodate particle-sampling probes, 6-inch-diameter bosses with 4-inch openings into the tunnel were attached to the tunnel surfaces at sampling stations 2, 4, and 6. The bosses are located approximately 30 degrees away from the bottom of the tunnel. Cover plates close the openings when not in use.

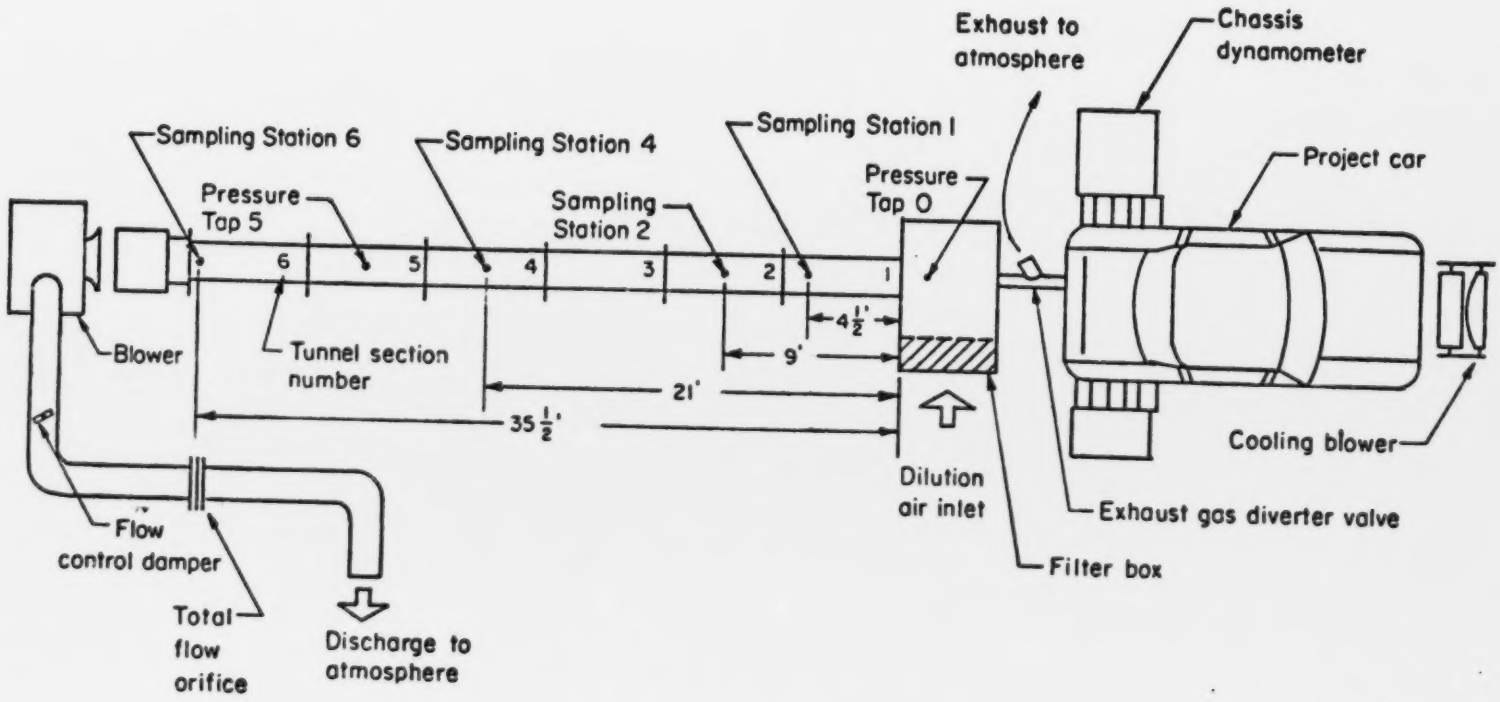


FIGURE 3. ORIGINAL LAYOUT OF DILUTION TUNNEL, WITH INDUCED DRAFT BLOWER

Velocity and Gas Mixing Profiles

Velocity profiles in the dilution tunnel were measured at the major sampling stations at two tunnel flow rates and two exhaust-gas flow rates, using shop air to simulate the exhaust gas flow. The velocity measurements were made with a Thermal Systems, Inc., anemometer using a hot-film sensor projecting into the air stream. Mixing profiles were determined at 580 feet per minute using CO as a tracer gas added to the simulated exhaust gases and a Beckman NDIR CO Analyzer to measure the CO concentrations in the tunnel.

Both velocity and mixing profiles were measured by traverses of probes in vertical and horizontal planes. In each traverse, 14 positions were measured for the velocity profiles and 15 positions for the mixing profiles. Tests were run separately for horizontal and vertical velocity traverses, without attempting to adjust flow to exactly the same value in each test.

Figure 4 shows the velocity and mixing profiles measured at Station 6. These curves show that mixing of exhaust gases and dilution air was good and that velocity profiles were satisfactorily flat in the cross section up to eight inches from the center line of the tube.

The velocity and mixing profiles were not affected by changes of "exhaust-gas" flow rate.

Aerosol Mixing Profiles

Mixing analyses were repeated with an aerosol at the high flow velocity used in the gas mixing studies above, in order to determine the variation in concentration of the aerosol particles across the vertical and

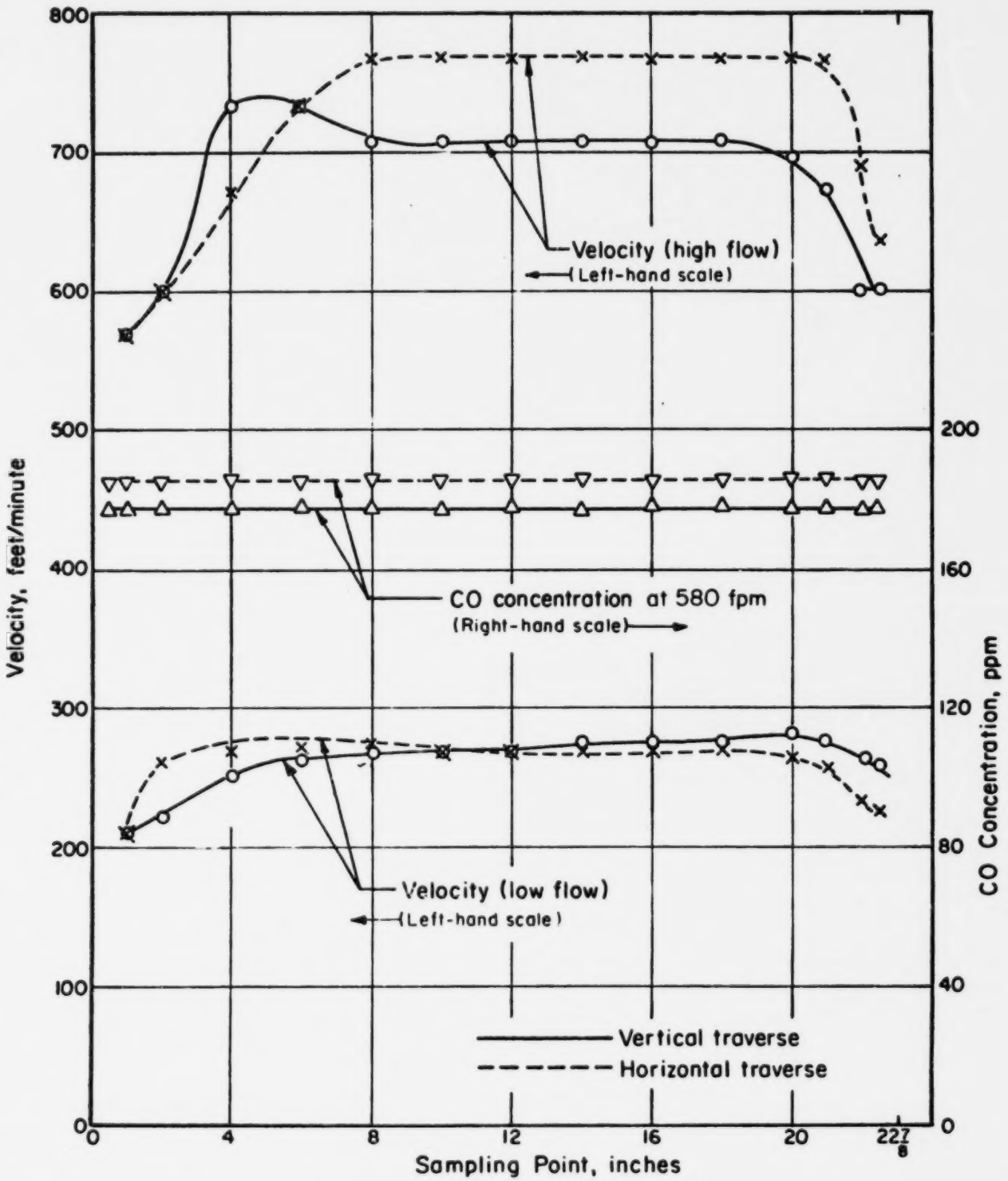


FIGURE 4. VELOCITY AND MIXING PROFILES AT SAMPLING STATION 6.

horizontal tunnel profiles. The sampling probe assembly (Figure 5) was a ring bolted between any two tunnel sections to hold 13 fixed sampling tubes, 3/8 inch in diameter, at the center and on vertical and horizontal axes at 5-, 8-, and 10-1/2-inch radii. The exit ends of the tubes were connected to absolute filter holders. Each filter holder contained a critical flow orifice which was designed for 0.5 ± 0.01 cfm, and was connected to a vacuum line.

During these profile studies, the sampling probe assembly was placed between the tunnel sections and the air velocity in the duct was adjusted to 580 ft/min, a velocity intermediate between the two values for high and low flow. The test aerosol was introduced in place of the automobile exhaust. A conventional aerosol can was used to discharge fluorescent dye dissolved in Freon-12 and toluene. The particle size of the aerosol was determined with the Battelle cascade impactor for each run and was varied from run to run between 0.87 to 5.9 μm mass-mean diameter by varying the dye concentration. The amounts of dye collected on each impaction stage and on the absolute filter were determined with a fluorophotometer.

Table 2 is a summary of the measurements at 5-1/2, 17-1/2, and 29-1/2 feet from the point of aerosol generation. The data show that the greatest deviation was obtained in the larger particles at the first sampling point. The coefficient of variation of the mean (the normalized standard error) was less than 4 percent for any test and averaged less than 2 percent.

Figures 6, 7, and 8 show plots of the mass variation of dye concentration for the 0.87, 2.0, and 5.9 micron dye aerosols for three sampling positions. The variation for the 5.9 micron particles at the first sampling station was greater than all others.

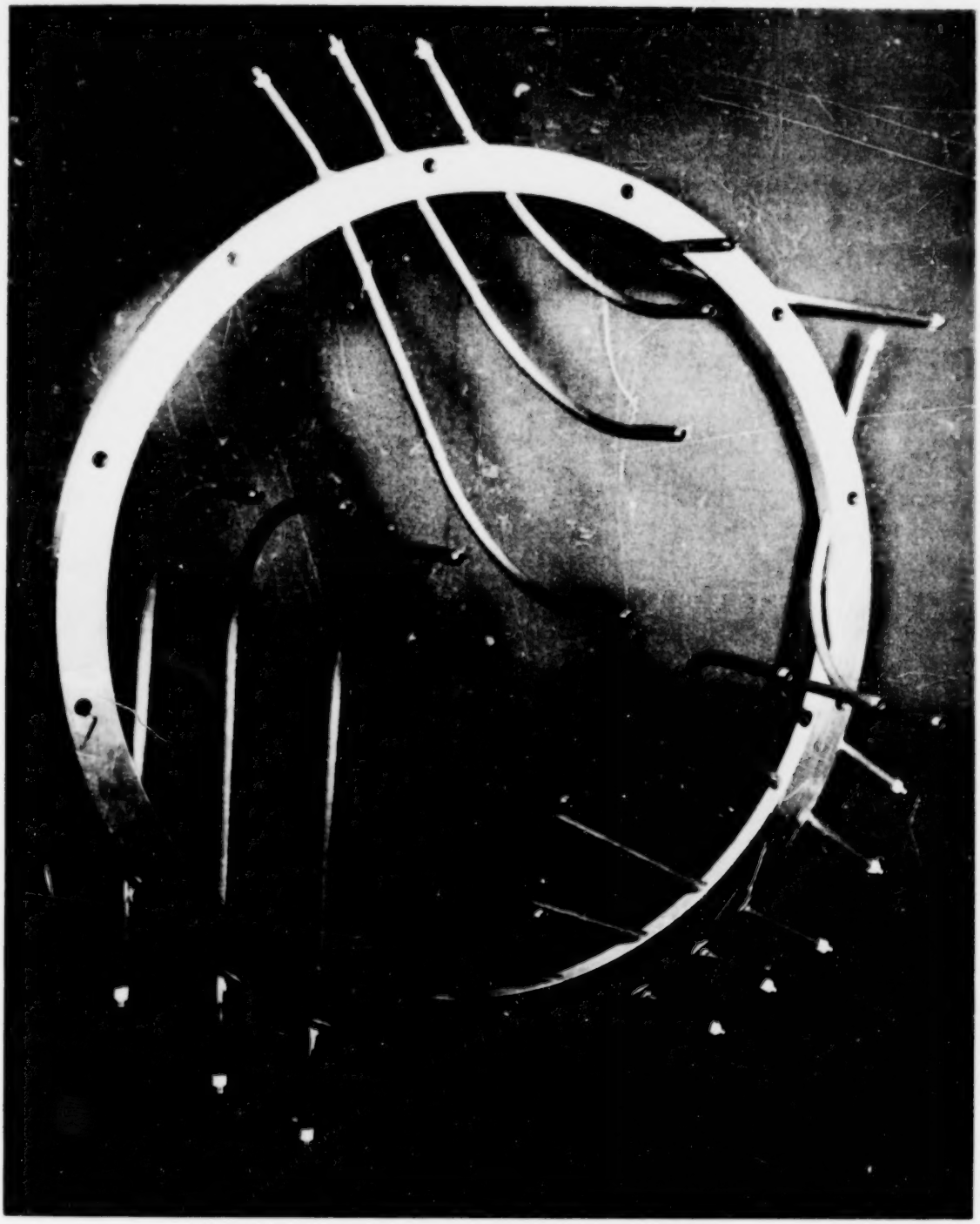


FIGURE 5. SAMPLING PROBE ASSEMBLY USED FOR AEROSOL MIXING STUDIES IN THE DILUTION TUNNEL

TABLE 2. DETERMINATION OF AEROSOL CONCENTRATION PROFILES IN THE DILUTION TUNNEL AT 560 FPM

Travel Distance, feet	Size MMD[a], μm	Concentration AMC[b], $\bar{x}$	Distribution SD[c], σ	Distribution SEM[d], $\sigma/\sqrt{n}$	Coefficient of Variation of the Mean, percent
5 1/2	0.87	109.8	3.77	1.04	0.05
5 1/2	2.0	434.5	30.4	8.44	1.95
5 1/2	5.9	206.5	26.5	7.35	3.56
17 1/2	0.85	239.2	12.5	3.61	1.51
17 1/2	1.3	237.8	14.5	4.17	1.76
17 1/2	2.0	446.1	19.8	5.5	1.23
17 1/2	2.8	617.5	35.8	9.9	1.61
17 1/2	3.6	333.3	22.1	6.6	1.98
17 1/2	5.9	325.3	15.5	4.31	1.33
29 1/2	0.87	266.8	18.3	5.07	1.90
29 1/2	2.0	358.2	14.7	4.08	1.14
29 1/2	5.9	438.5	34.2	9.5	2.17
29 1/2	5.9	463.1	26.6	7.4	1.59

(a) Mass Mean Diameter.
(b) Arbitrary fluorescent units (proportional to microgram/m^3).
(c) Standard Deviation.
(d) Standard Error Mean.

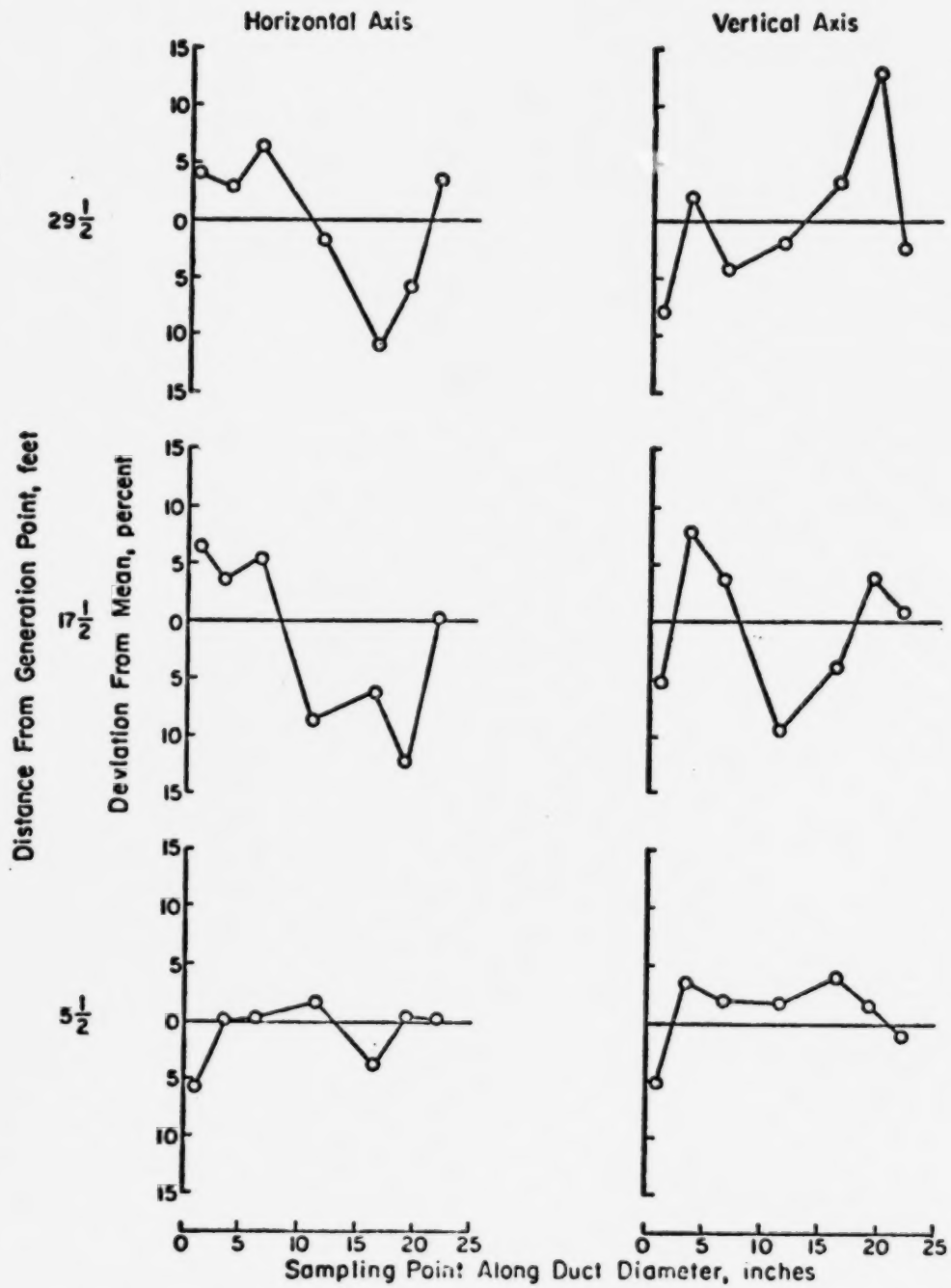


FIGURE 6. DILUTION TUNNEL MIXING PROFILES FOR AEROSOLS 0.87 MICRON IN DIAMETER

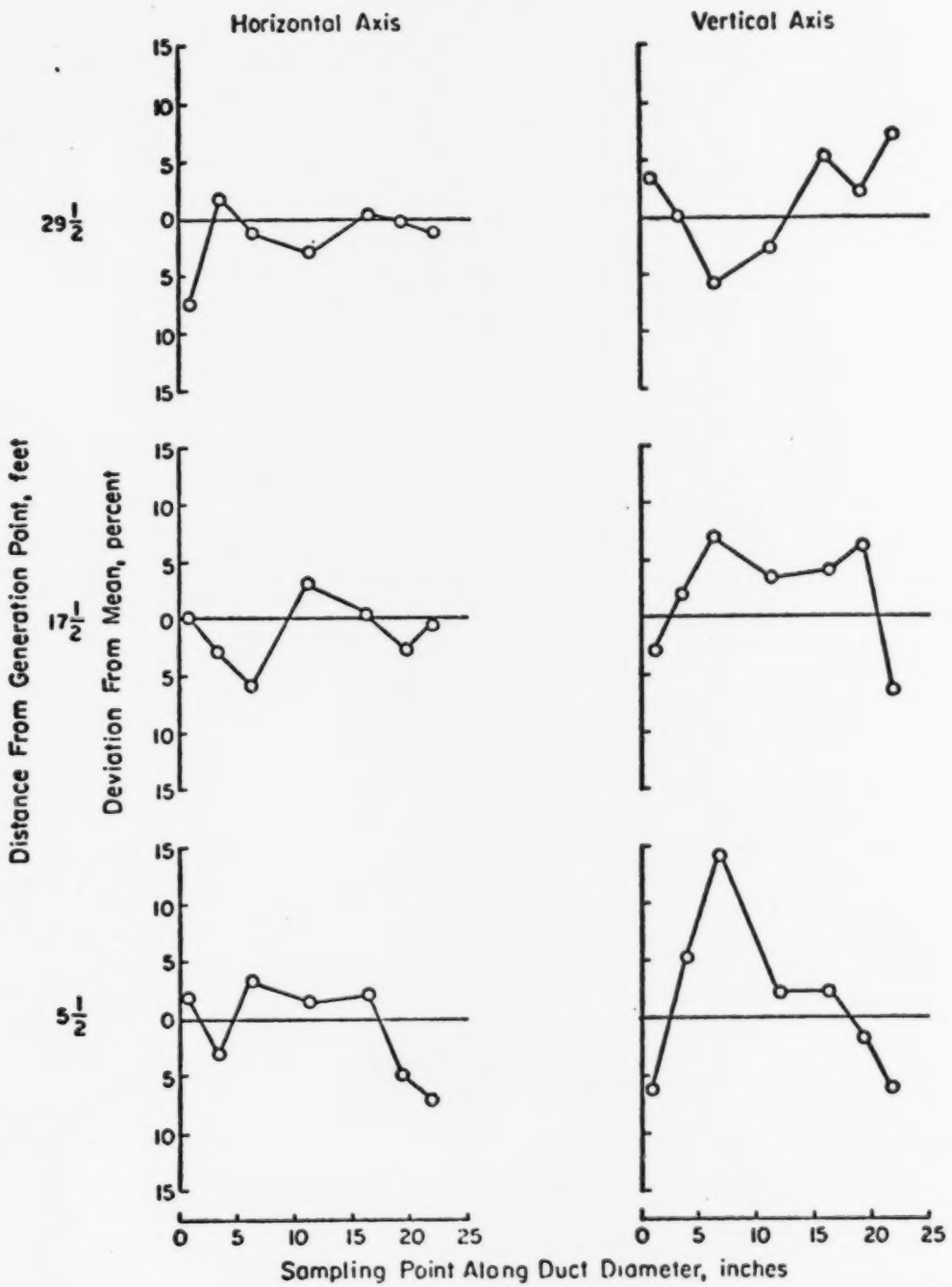


FIGURE 7. DILUTION TUNNEL MIXING PROFILES FOR AEROSOLS 2.0 MICRONS IN DIAMETER

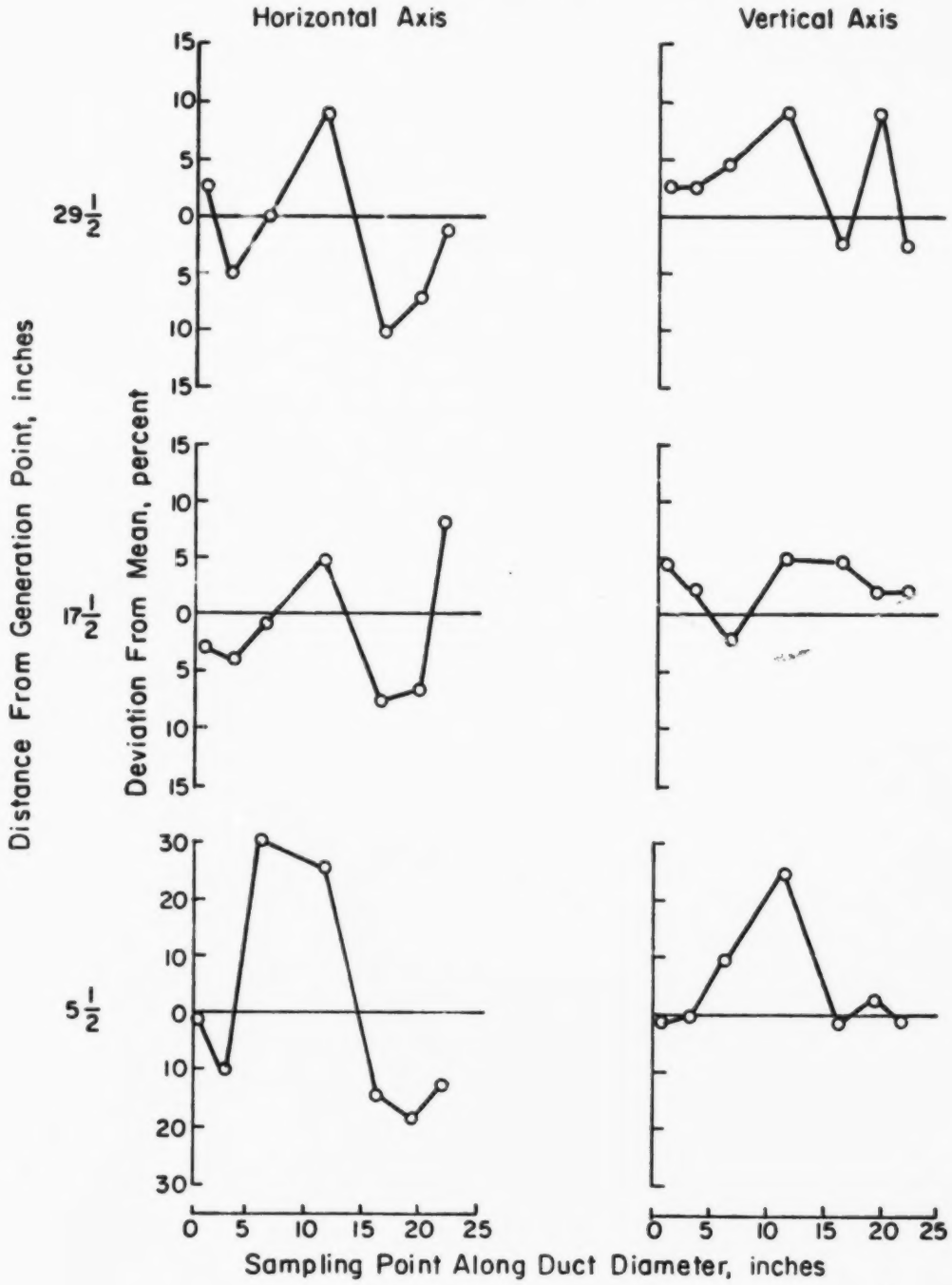


FIGURE 8. DILUTION TUNNEL MIXING PROFILES FOR AEROSOLS 5.9 MICRONS IN DIAMETER

Modification of the Dilution Tunnel

Positive Pressure Operation

The original dilution tunnel arrangement, shown in Figure 3, had the blower located at the tunnel exit to induce air flow, which gave a negative pressure in the tunnel. With this configuration, it would be difficult to pull a sample from the tunnel to be transferred to a residence chamber without affecting the particulates, so the tunnel was modified according to suggestions received from Dr. John B. Moran[1]. The blower was replaced with a smaller 1600 cfm blower installed at the inlet to produce a positive pressure in the tunnel which would serve to force a portion of the diluted exhaust gases into the residence chamber. The new blower has adequate capacity to supply up to 1200 cfm nominal dilution flow at 1-inch H_2O positive pressure for modified LA-4 cycle operation.

Change in Dilution Ratio

The modified tunnel is operated with a flow of 900 scfm to give a 30:1 dilution ratio for the modified LA-4 cycle rather than at the previous 20:1 ratio. It is then possible to achieve more easily a final dilution of 300:1 in the residence chamber described below.

Aerosol Mixing Profile

The aerosol profile in the modified dilution tunnel under positive pressure was measured at the 29-1/2-foot position, as described above. In this case, the automobile was running on the chassis dynamometer at a steady 35-mph and 3-hp as the dye was introduced.

---

(1) Consultation with Dr. Moran, EPA-NERC, Division of Chemistry and Physics, Research Triangle Park, North Carolina 27711.

The uniformity of distribution of the aerosol on the filters is shown in Table 3. The variations were minor and the exhaust was considered to be mixed essentially completely throughout the cross-section of the tunnel. Nonuniform dispersion of particles within the tunnel is not, therefore, a major source of sampling error.

Residence Chamber

Figure 10a shows a perspective view, Figure 10b shows the layout of the test apparatus with a residence chamber placed at the end of the positive-pressure dilution tunnel, and Figure 10c shows details of residence-chamber probes and purge system. The residence chamber was constructed of 6-mil black polyethylene film with heat-sealed seams. Its dimensions are about 9 ft. x 12 ft. x 20 ft. for a filled volume of about 2100 cu ft. The flexible chamber is suspended within a lightweight external framework, and the bottom is supported by an independent frame which can be raised to partially collapse the chamber for purging. While diluted exhaust gases are fed into the chamber the botton frame is lowered as required to maintain a constant back pressure on the proportional sampling system.

In the circulation and sampling system, the purge blower (360 cfm at 1-1/4 inches static pressure) is used to purge the residence chamber after a run and to pass the new charge of chamber air through a particulate filter (99.97 percent efficiency at 500 cfm and 0.9 inches static pressure) a drier or humidifier, and an activated charcoal absorber, to control initial contamination and humidity in the chamber.

A 2-inch-inside-diameter PVC pipe was used to carry the sample from the tunnel to the chamber. For convenience in preliminary residence chamber studies, the line was installed temporarily in the tunnel between

TABLE 3. DISTRIBUTION OF DYE AEROSOL AT REPLICATE SAMPLING SITES

Filter Location[a]	Photometer Reading Arbitrary Units
1	80.5
2	81.2
3	80.5
4	78.3
5	83.0
6	79.4
7	85.6
8	78.0
9	76.4
10	85.5
11	74.0
12	75.5
13	82.3
σ = 3.59[b]	
Percent coefficient of variation - 4.48[c]	

(a) See Figure 9 for location diagram.

(b) $\sigma = \sqrt{\frac{\Sigma(\bar{R} - R)^2}{n-1}}$, where R is the arbitrary photometer reading.

(c) Percent coefficient of variation = $\frac{\sigma}{\bar{R}} \times 100$.

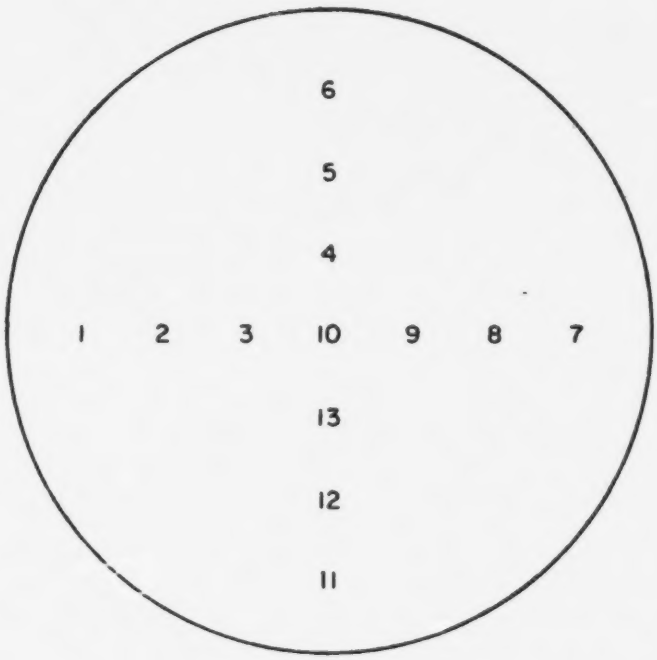


FIGURE 9. NUMBER CODE FOR SAMPLING PORT LOCATIONS, LOOKING TOWARD AUTOMOBILE

(See Table 3)

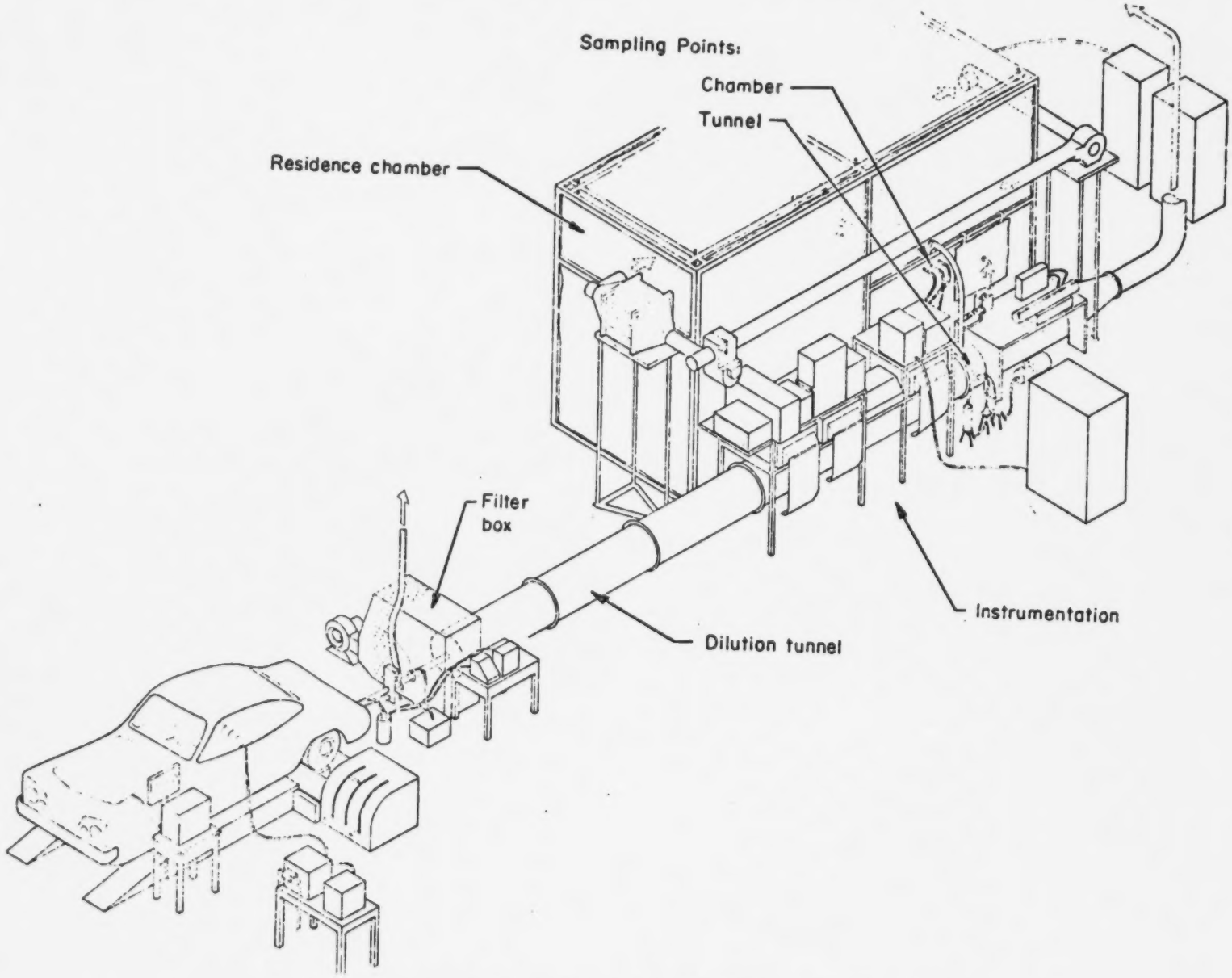


FIGURE 10a. MODIFIED TEST APPARATUS WITH POSITIVE PRESSURE SAMPLING

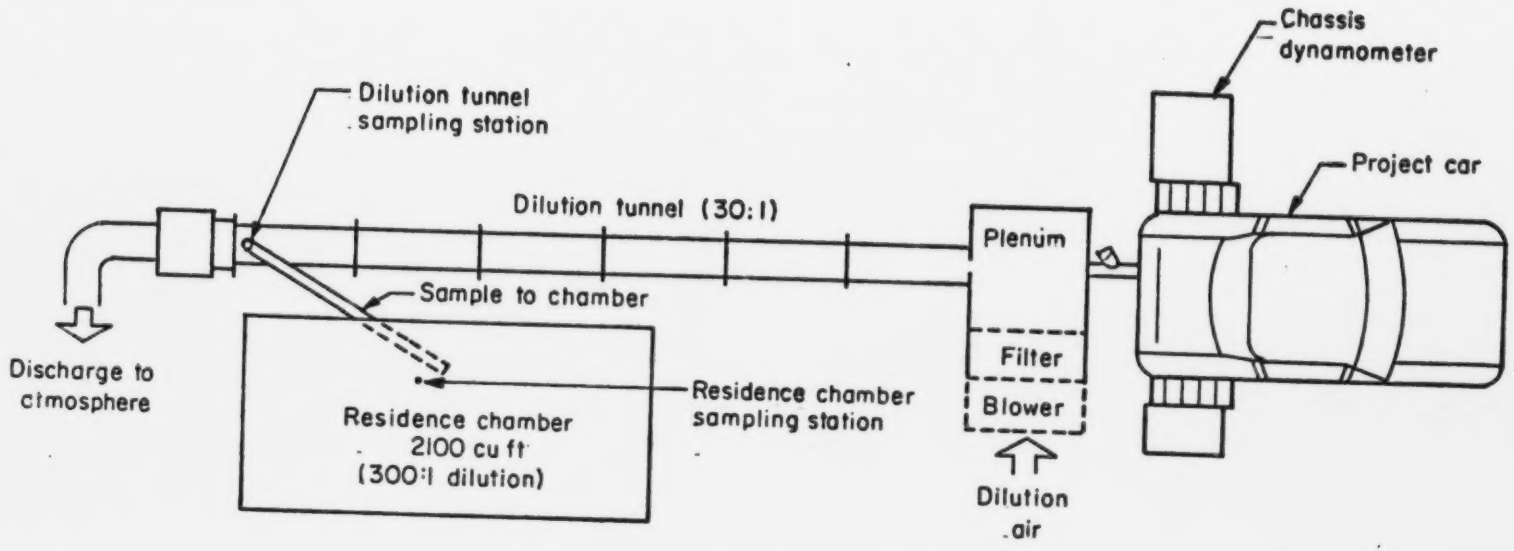


FIGURE 10b. MODIFIED LAYOUT OF TEST APPARATUS WITH POSITIVE PRESSURE SAMPLING

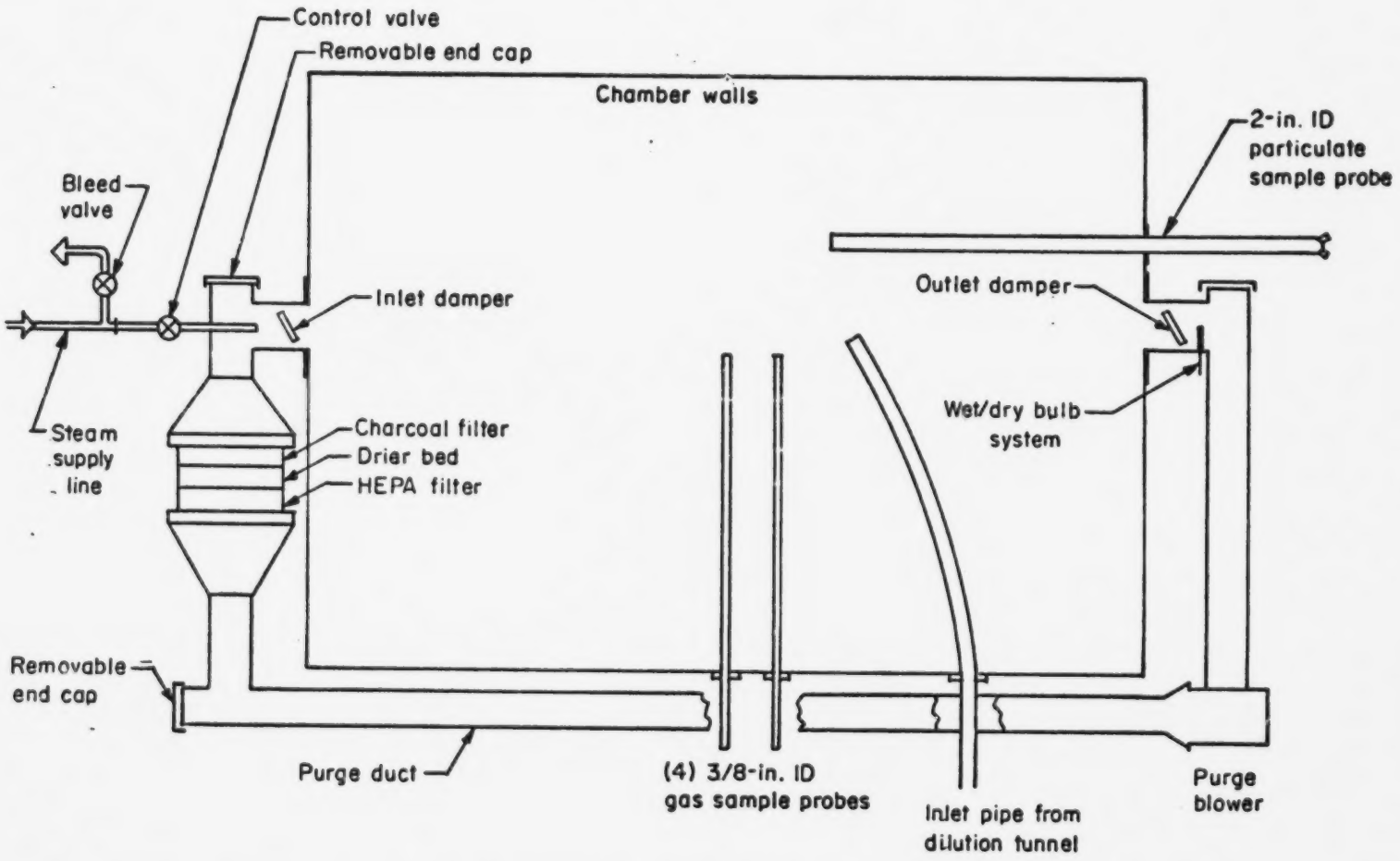


FIGURE 10c. LAYOUT OF RESIDENCE CHAMBER AND PURGE-CIRCULATION SYSTEM

sections 5 and 6, 30 feet downstream from the mixing orifice, and entered the chamber at one end 4 feet from the top, projecting 10 feet into the chamber. The total length of this sample line was about 30 feet with two 90-degree elbows. The sample-flow velocity through the line was enough to prevent most particles less than 4 or 5 microns from depositing on surfaces. The final sample line was much shorter and entered the chamber from the side as shown in Figure 10a.

Sampling from the residence chamber for particulate collection, for visibility measurements, and for gas analysis is done through two 1/2-inch stainless steel probes extended into the center of the chamber.

The sample line from the dilution tunnel to the residence chamber is a 2-inch ID plastic (PVC) pipe with the probe's inlet reduced for isokinetic sampling.

Apparatus for Aerosol Monitoring

Filters and Impactors

The basic apparatus used to determine the particulate loading of the diluted automobile exhaust includes absolute filters and impactors. The particulate samples were collected on various types of filters contained in 47-mm and 142-mm-diameter filter holders. These filter holders were equipped with critical-flow orifices which were calibrated for a 1.0 cfm flow rate.

Two types of impactors (the Andersen and a special Battelle impactor) were used. The Andersen impactor was purchased late in this year's program and few data were obtained with it because the large mass of the collection surfaces made accurate weighing difficult. Thin shim stock was then obtained for use as impaction slides in subsequent tests.

A special cascade impactor was designed and constructed for particle size analysis of the exhaust particulates. This impactor has a sampling rate of 1.0 cfm and uses a critical flow orifice to fix the flow and particle-size cut-off on the last stage. The cut-off size of this stage is 0.25 micron. Cut-off sizes of the upstream stages increase by a factor of two for each successive stage from 0.25 to 16 microns. The material smaller than 0.25 micron is collected on an absolute filter (76-mm diameter, active area 21.2 cm^2). The major advantage of this impactor is that it has an unusually sharp classification, so that greater precision is possible in particle size classification for the submicron aerosol particles which comprise the bulk of the automobile exhaust from the relatively new automobile engines.

Single Particle Counter

In order to detect slight changes in the particle size of an aerosol, it is necessary to compare two measurements of a large particle population within a fairly short time interval. To achieve this goal, a single-particle counter was assembled at Battelle, and was used to study these auto exhaust aerosols.

Basically, the instrument consists of the optics section from a Bausch and Lomb Dust Counter, a signal processor, and a multi-channel analyzer. In operation, the aerosol particles are passed through a light-scattering cell and the scattered light is monitored by a photo multiplier tube. When only one particle at a time passes through the small view volume, it is possible to measure the amount of light scattered by it and to classify it according to the amount of energy received by the photo multiplier tube.

The larger the particle, the greater the quantity of light scattered. A measure of relative particle size is obtained.

Figure 11 is a photograph of the assembled particle counter. The particle counter is shown in the lower right portion of the photograph. The filter circuit and the signal processor circuit are in the two boxes to the left of it. Other apparatus shown consists of the automatic timer, computer memory, amplifier, printer, and high speed analog-to-digital converter. During operation, it is possible to view the pulses as they are being counted on the oscilloscope. An automatic printer permanently records the data after any selected time period.

As a preliminary check to determine if the apparatus functioned properly, a pulse simulating a particle was passed through the system and was recorded by the multichannel analyzer. This pulse was attenuated by about 3 decibels for each trial check, representing progressively smaller sizes. Figure 12 is a log-log plot of the pulse voltage versus the channel in which the pulse was counted which is straight between Channels 10 and 125.

The calibrating procedure to relate particle size to pulse voltage used aerosols prepared from various Dow Polystyrene Latices of uniform particle size. The polystyrene latices were diluted with distilled water and atomized into a large Mylar bag using a medical nebulizer. Many of the atomized droplets contained no particles and very few contained more than one. After the water evaporated, the bag contained a mono-dispersed polystyrene aerosol of the characteristic particle size. The aerosols were sampled through the single-particle counter with the output of the photomultiplier tube fed into the 256-channel analyzer.

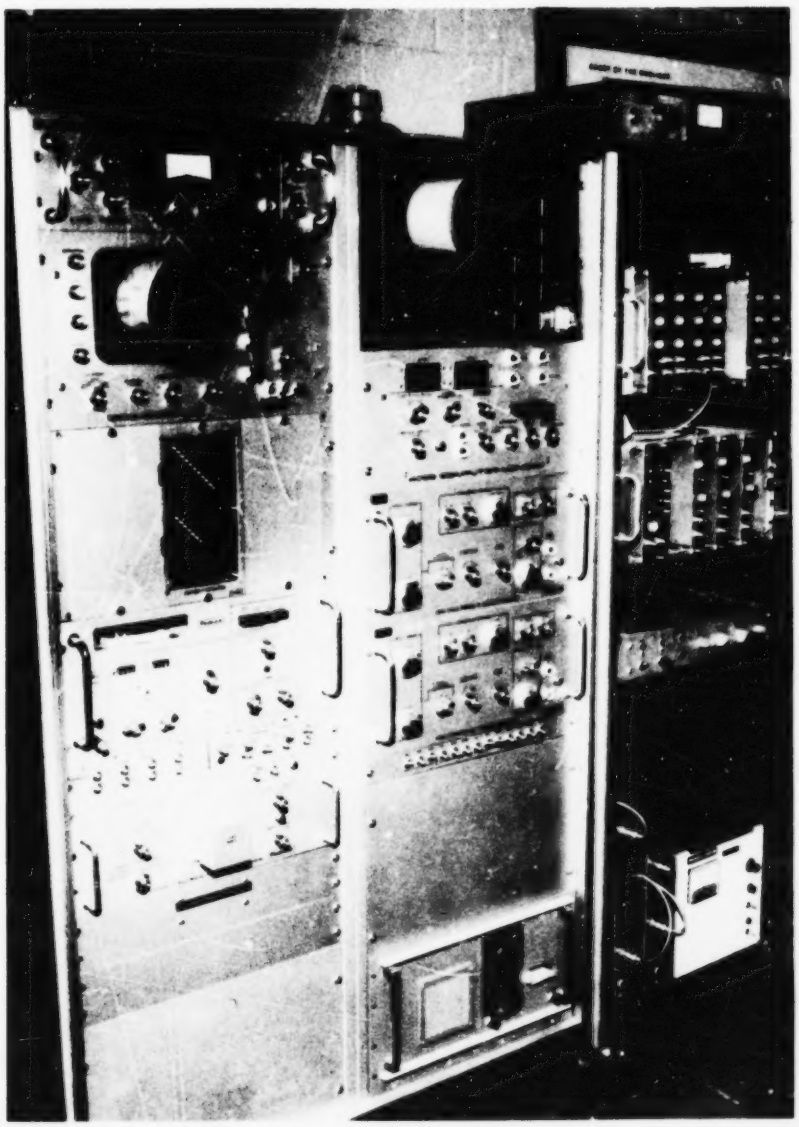


FIGURE 11. PHOTOGRAPH OF SINGLE-PARTICLE COUNTER

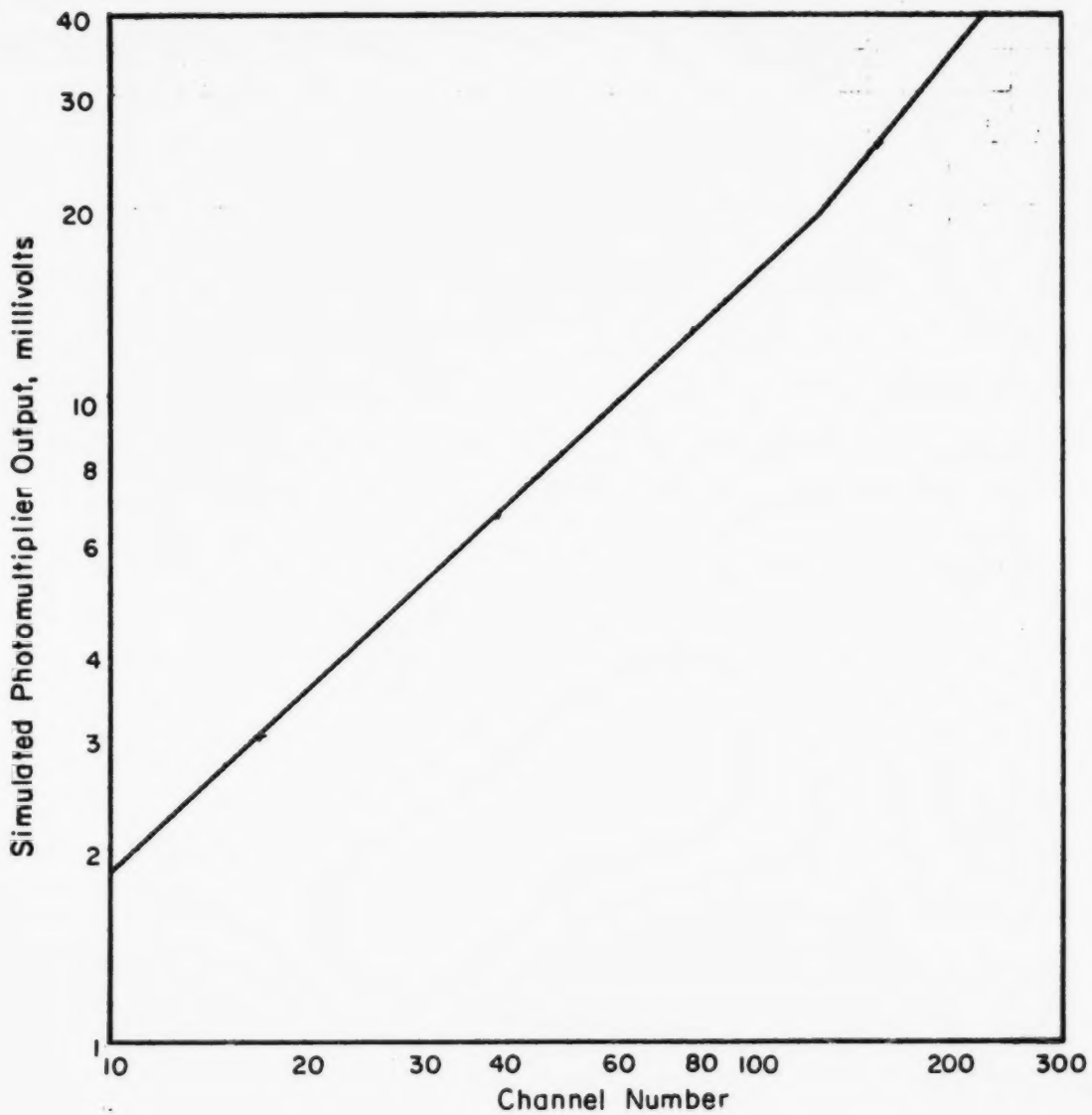


FIGURE 12. CALIBRATION OF SINGLE PARTICLE COUNTER WITH SIGNAL GENERATOR

Figure 13 is a plot of the data. In order to cover the entire particle size range of interest, it was necessary to use two different scales of the B & L Particle Counter. The photomultiplier output for particles larger than 1.5 microns is proportional to the 1.64 power of the particle diameter, whereas for particles smaller than 1.0 μ, the output is proportional to the particle diameter to the 0.55 power.

The particle counter was not calibrated for automobile exhaust, because it would be difficult to measure the size distribution of exhaust and to stabilize a sample for use as a standard calibration mixture. However, the particle counter does measure particle concentration of each channel and shows shifts in particle size or changes in light-scattering properties during a long-term residence test.

EXPERIMENTAL RESULTS AND DISCUSSIONS

Comparative Measurements of Vehicles

Gaseous Emissions From Steady-State Operation

At intervals during break-in of each of the two vehicles, hydrocarbon (HC) and carbon monoxide (CO) concentrations in the exhaust gas were measured at 50-mph steady state, with nonleaded fuel No. RE-141A. The results for the white car are presented in Table 4, and for the blue car in Table 5.

There was no significant progressive change in the exhaust emissions of the white car. The HC and CO concentration levels at the beginning point (110 miles) and at the end point (3930 miles) were the same. The HC concentration at about 970 miles was almost 40 percent above the

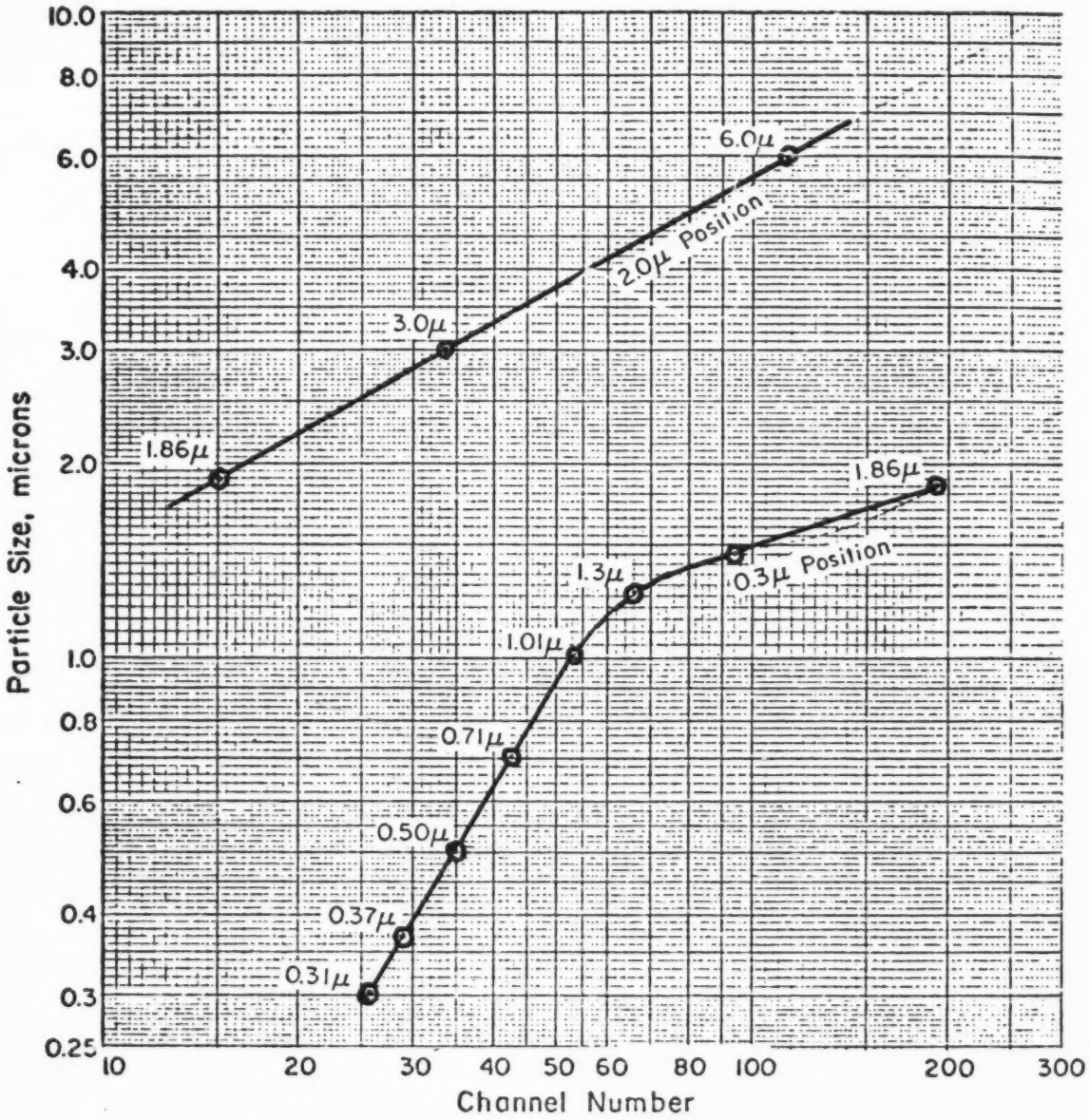


FIGURE 13. CALIBRATION OF SINGLE PARTICLE COUNTER WITH POLYSTYRENE LATICES

TABLE 4. EXHAUST GAS COMPOSITION FROM THE EXHAUST PIPE AT 50-MPH STEADY CRUISE DURING CONDITIONING OF WHITE CAR (UNLEADED FUEL)

Accumulated Miles	HC Concentration, ppm C	CO Concentration, percent	Manifold Air Pressure, in Hg	Exhaust Gas Temperature, F
110	1100	0.7	17.0	440
577	1095	0.7	-	458
706	1065	0.6	-	456
919	1395	1.0	18.7	462
1480	1050	0.8	-	462
1705	990	0.8	18.9	462
1720	1080	0.7	-	438
1940	1127	0.9	-	463
2200	1050	0.8	-	462
2425	1050	1.45	-	467
2590	1005	0.9	-	465
2704	1050	-	-	469
3045	1050	0.8	-	458
3374	660	1.2	-	462
3600	795	1.6	-	466
3760	900	0.7	19.2	480
3893	990	0.75	18.5	424
3912	1050	0.55	-	424
3920	1050	0.5	18.5	404
3930	1080	0.75	18.5	446

TABLE 5. EXHAUST GAS COMPOSITION FROM THE EXHAUST PIPE AT 50-MPH STEADY CRUISE DURING BREAK-IN OF BLUE CAR (UNLEADED FUEL)

Accumulated Miles	HC Concentration, ppm C	CO Concentration, percent	Manifold Air Pressure, in Hg	Exhaust Gas Temperature, F
58	750	0.6	18.8	454
602	885	1.07	19.1	-
770	810	1.15	19.2	-
953	750	0.95	19.2	-
1938	970	0.8	19.4	-
2176	1100	0.7	19.5	-
2476	980	0.5	19.5	-
2629	1042	0.6	19.5	-
2745	1027	0.6	19.5	-
2946	900	0.7	19.5	-
3174	1065	0.75	19.4	-
3394	1080	0.7	19.5	430
3674	975	0.7	19.4	490

average, and 560 miles later has dropped nearly to the average. The cause is not known. The low HC concentration value at 3375 miles (about 40 percent below the average) followed a two-week lay-off period. During the next 500 miles, the HC concentration rose again to the average value.

HC emissions from the blue car increased 40 percent during the first 2000 miles, at which point the concentration was nearly the same as the white car. At 4000 miles, HC emissions from the blue car had increased 60 percent.

For the next 4000 miles, the blue car was fueled with leaded fuel No. RE-141C and the white car was fueled with unleaded fuel No. RE-141B. During this period, hydrocarbon analyses were performed periodically under 50-mph steady-state conditions. Figure 14 shows a comparison of hydrocarbon emissions from the two vehicles. The HC emissions for the white car did not change significantly in 4000 miles of additional operation on unleaded fuel but the HC emission from the blue car, operated with leaded fuel, increased an additional 90 percent, so that at 9000 miles, HC emission was three times higher than at the beginning.

Gaseous Emissions From Modified LA-4 Cycles

Integrated bag samples were collected from the dilution tunnel during single modified LA-4 cycles on unleaded gasoline RE-141B. Both overnight soak (about 17 hours) and rapid cooldown cycles were run. A large (about 12 cubic foot) polyethylene bag was used with a vacuum pump drawing a sample from the tunnel at a rate of about 1/2 cfm. The tunnel flow was 600 cfm.

Table 6 presents the results of these tests. Emissions after rapid cooldown or overnight soak were the same.

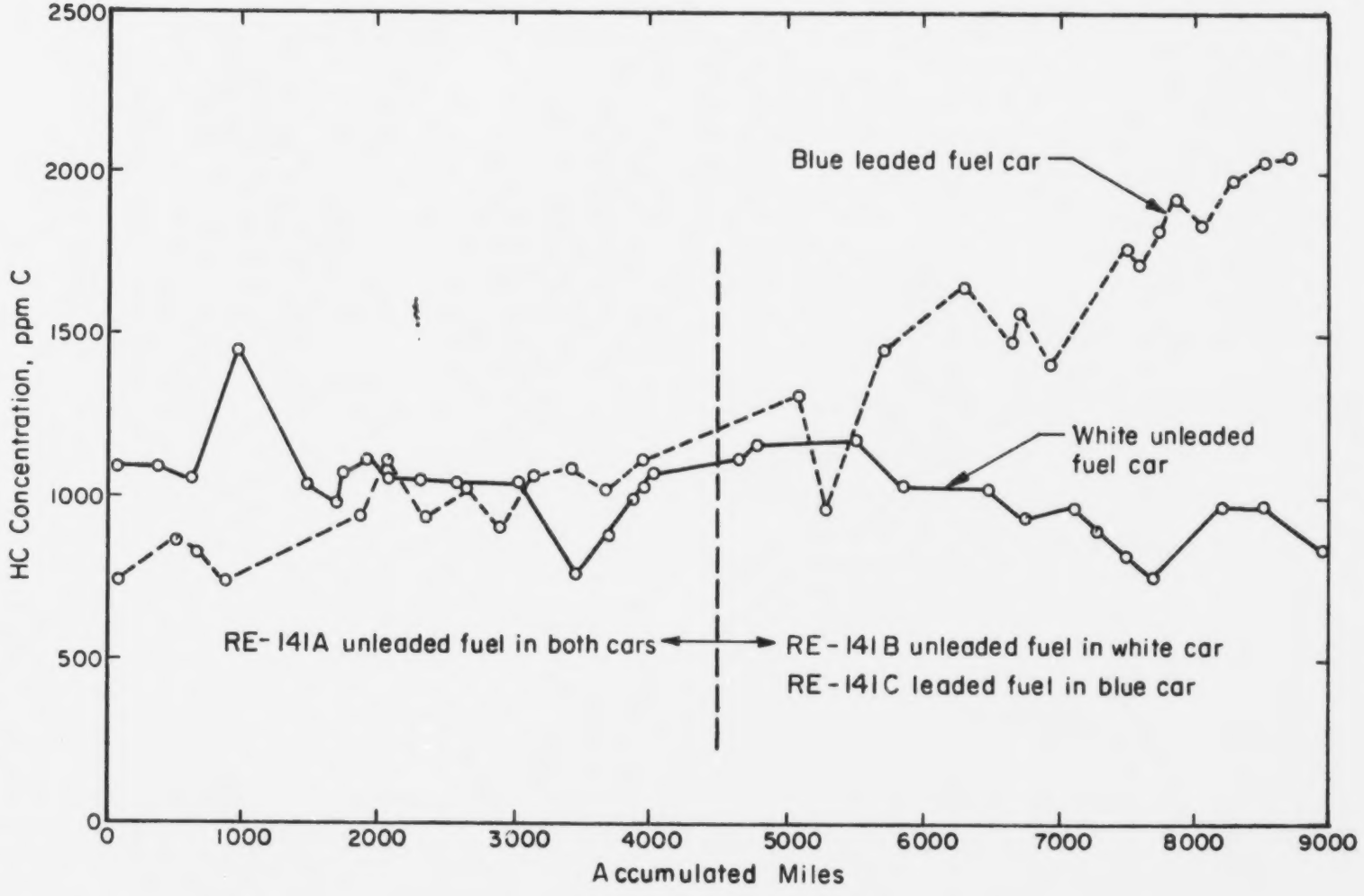


FIGURE 14. HC CONCENTRATIONS SAMPLED FROM THE EXHAUST AT 50 MPH STEADY CRUISE DURING BREAK-IN OF PROJECT CARS

TABLE 6. COMPOSITIONS OF INTEGRATED EXHAUST SAMPLES FROM SINGLE MODIFIED LA-4 CYCLES

Vehicle	Test No.	HC[(a)], ppmC	HC[(a)], g/mi	CO, ppm	CO, g/mi	NO_x, ppm	NO_x, g/mi	Conditions
Blue Car	1	61	1.9	167	9.9	5	0.32	Overnight soak
	2	-	-	150	8.9	-	-	Overnight soak
	3	45	1.4	100	5.9	-	-	Rapid cooldown
White Car	1	31	1.0	110	6.5	4	0.25	Overnight soak
	2	36	1.1	125	7.4	4	0.25	Rapid cooldown
	3	38	1.2	75	4.4	5	0.32	Overnight soak
	4	24	0.8	50	3.0	4	0.25	Rapid cooldown
	5	72	2.3	150	8.9	-	-	Overnight soak
	6	44	1.4	175	10.0	-	-	Rapid cooldown

(a) Instruments were calibrated to read concentrations in ppm.

Conversion factor: $g/mi = 600 \frac{ft^3}{min} \times \frac{23}{7.5} \frac{min}{mi} \times 0.0283 \frac{m^3}{ft^3} \times (ppm) \frac{cm^3}{m^3}$

$$\times \frac{1}{24700} \frac{GMV}{cm^3} \cdot \frac{(MW)}{1} \frac{n}{GMV} = 2.11 \times 10^{-3} \text{ (ppm) (MW)}.$$

Inorganic Composition of Exhaust Particulates

Exhaust particulates from unleaded fuel were sampled at 1 cfm from the tunnel during one modified LA-4 cycle after 20:1 dilution by filtered air. The quantities of inorganic elements collected on the Milipore filters were measured at very low concentrations (at the μg level) by optical emission spectroscopy. The quantitative accuracy of these measurements is about ± 50 percent, but at such low concentrations, this degree of uncertainty is not significant. Furthermore, the filtered dilution-tunnel air stream without exhaust particulates contains the same elements in about the same low concentrations as the background concentrations in filtered air, as shown in Table 7.

Morphology of Exhaust Particles

The particle types and size ranges for both cars were the same when both cars were fueled with unleaded gasoline. Primarily, there are three types of particles: carbon black, tar droplets, and pyrolyzed chunks of carbonaceous material. The pyrolyzed material was the least prevalent emitted from both cars. Typical particles resembling carbon black and tar droplets are shown in Figures 15 and 16. Almost all of the exhaust particles were smaller than 1.0 μ.

By the criterion of particle morphology, the two engines perform very similarly.

Organic Analysis of Exhaust Emissions by HPLC and GC

After break-in of the project cars on unleaded fuel RE-141A, the cars were run through modified LA-4 cycles and at 50-mph steady-state to

TABLE 7. COMPARISON OF INORGANIC COMPOSITIONS OF PARTICLES COLLECTED FROM THE DILUTION TUNNEL

(Micrograms per filter[a] after passing 23 cu. ft. sample at 1 cfm)

	Pb	Zn	Si	Fe	Mg	Al	Ca	Cu
Filtered dilution tunnel air only[b]	<0.5	<0.5	3.0	0.5	1.0	0.5	3.0	1.0
Exhaust from unleaded fuel in blue car sampled from dilution tunnel[c]	<0.5	<0.5	2.0	0.3	2.0	1.0	5.0	0.5
Exhaust from unleaded fuel in white car sampled from dilution tunnel[c]	<0.5	<0.5	3.0	1.0	2.0	0.5	5.0	0.5

(a) Millipore membrane filter, 47-mm diameter.

(b) Background particles in the filtered tunnel air. Not significantly different from inorganic particles collected during operation of the modified LA-4 cycle.

(c) To convert reported values of micrograms per filter into equivalent g/mile of car operation, multiply by factor

$$600 \times \frac{1}{7.5} \times 10^{-6} = 84{:}10^{-6};$$

e.g. Ca collected = $5.0 \times 84 \times 10^{-6} = 4.2 \times 10^{-4}$ g/mile.

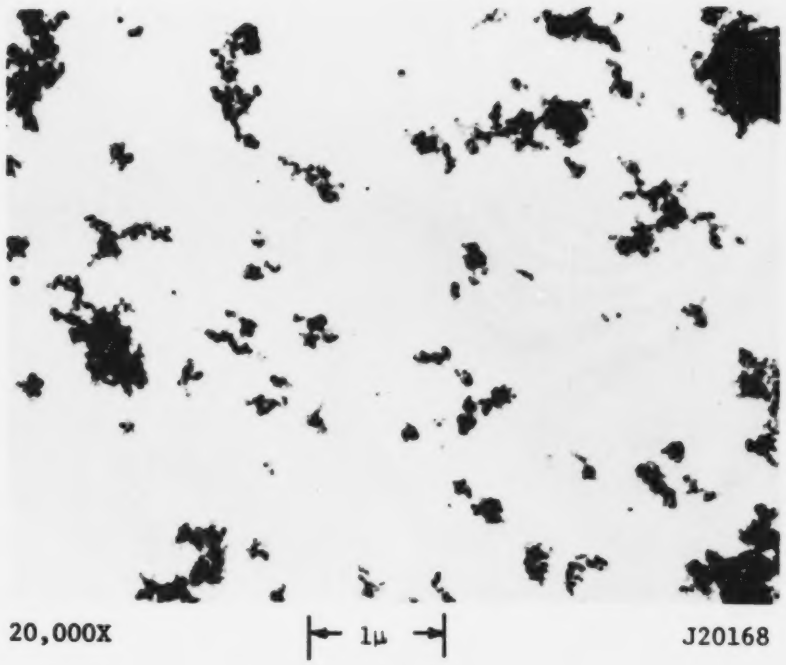


FIGURE 15. TYPICAL CARBON-BLACK-TYPE EXHAUST PARTICLES FROM UNLEADED FUEL COLLECTED FROM THE TUNNEL ON 0.25 μm STAGE OF IMPACTOR

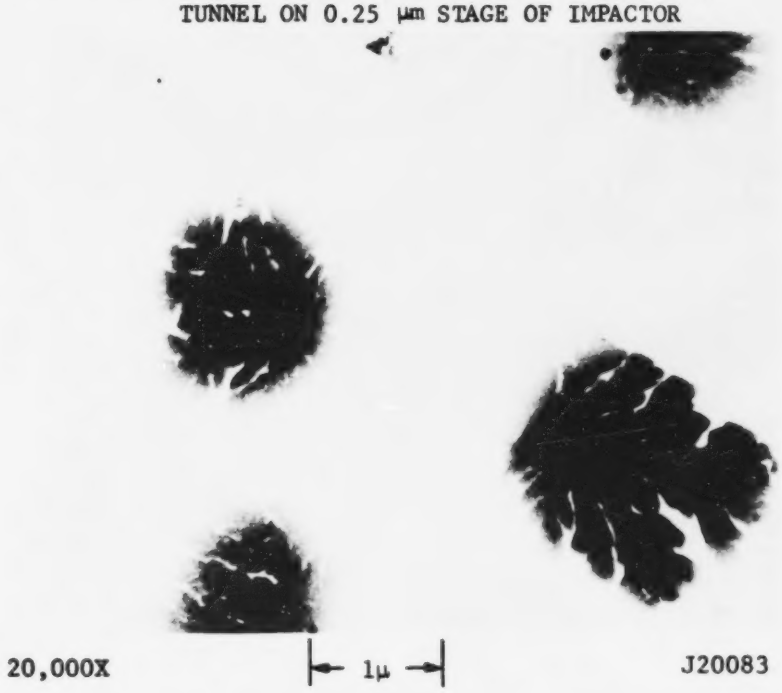


FIGURE 16. TYPICAL TAR-DROPLET-TYPE EXHAUST PARTICLES FROM UNLEADED FUEL COLLECTED FROM THE TUNNEL ON 0.5 μm STAGE OF IMPACTOR

generate samples for organic analysis by high-pressure liquid chromatography (HPLC) and gas chromatography (GC). First, fuel RE-141A, then RE-141B, was used to generate samples for organic analysis. In the set of runs with fuel RE-141B, a 1967 Chevrolet was also used to generate particulate to determine if the organic fraction from its exhaust differed from that of the white and blue cars.

Exhaust particulate matter was collected from the tunnel on glass fiber filters, and the filters were extracted in Soxhlet apparatus with methylene chloride. Concentrates were transferred to small aluminum pans (~5 mg tare), dried, and weighed on an electrobalance, after which solutions were prepared for analysis by HPLC and GC. Gas chromatograms were developed using a 10 ft x 1/8-inch (stainless steel) column of OV-17 on "Gas Chrom Q" solid substrate. The temperature was programmed from 100 C to 250 C at 6/C minute. For HPLC, Waters Associates ALC-100 Analytical Liquid Chromatograph was used with a 9 ft x 1/8-inch column of oxyproprionitrile (OPN) on Porasil and with a mobile phase of 0.25 percent isobutyl ketone in isooctane. Peak detection for HPLC was accomplished by ultraviolet photometric monitoring at 254 nm.

Extracts from exhaust particulates generated under different operating conditions and by different cars were examined by both HPLC and GC and the chromatograms were compared to identify any compositional differences. Such comparisons would indicate, along with other diagnostics, operating similarities or differences between the two cars. In order to evaluate the ability of these techniques to detect compositional differences, the exhaust particulate from a 1967 Chevrolet automobile was also carried through the same analytical procedures, and the data were compared with those for the two matched project cars.

Analyses by HPLC of particulate extract from the three cars are summarized in Table 8. All cars were operated for two consecutive modified LA-4 cycles using unleaded gasoline RE-141B, and with the choking action not under positive control after the cold start. Several major components are common to all samples but the ratios of these components varied widely. Moreover, the differences between the two matched cars were no greater than those between repeated tests on either car alone. Furthermore, the same ratios for the 1967 car differed no more than those of the matched cars. Therefore, the organic composition of all the particulates as indicated by HPLC is similar, although the capabilities of the analytical method for detecting systematic differences is limited by the variability found in replicates.

Gas chromatography was also performed on exhaust particulate samples generated by the three cars operated on unleaded gasoline RE-141B. The gas chromatograms did not reveal significant compositional differences among organic components from the three vehicles. The particulate extract was shown to be a highly complex mixture with components eluting as a broad, largely unresolved envelope.

The chromatograms were made with the total organic fraction of the particulate, and the complexity of this organic mixture obscured compositional differences which might relate to differences in fuel composition or to engine operation. Complexity might be reduced by prefractionation of the total extract using techniques such as thin-layer chromatography or chemical separation. Such prefractionation would be advisable, if further samples are to be analyzed by gas chromatography.

TABLE 8. SUMMARY OF MAJOR PEAKS FOR FIVE HPLC CHROMATOGRAMS OF EXTRACTS FROM PARTICULATES

(Fuel, unleaded RE-141B; modified LA-4 cycles, cold start; sampled from tunnel at dilution of 20:1)

Automobile and Run Number														
Blue Car (#31)			Blue Car (#27)			1967 Car			White Car (#38)			White Car (#36)		
Retention Time, minutes	Approximate Peak Height	Attenuation	Retention Time, minutes	Approximate Peak Height	Attenuation	Retention Time, minutes	Approximate Peak Height	Attenuation	Retention Time, minutes	Approximate Peak Height	Attenuation	Retention Time, minutes	Approximate Peak Height	Attenuation
			1.5	21	X4									
			3.8	13	X4				3.5	43	X4	4.2	30	X4
									6.7	55	X8			
8.8	27	X32	8.6	79	X32	8.5	47	X32	9.4	33	X32	9.2	35	X32
11.7	69	X32	11.6	68	X64	11.4	38	X32	12.2	67	X8	12.1	49	X8
14.3	58	X16	14.2	45	X32	14.1	38	X8	15.1	82	X4	15.0	35	X8
19.2	43	X8	19.6	57	X8	18.8	68	X4	-	-	-	19.5	61	X16
									23.5	48	X8			
28.5	33	X4	29.8	78	X4	28.4	34	X4						

Exhaust Particle Sizes

Mass mean equivalent diameters (MMED) of exhaust particles were determined with removable film substrates laid in each stage of the Battelle cascade impactor. The material was collected during four (six in Run 42) cold start modified LA-4 cycles. Cumulative weight percent versus equivalent particle diameter is given in Figures 17 and 18 for each car. Both were fueled with nonleaded gasoline RE-141B. The mean size with unleaded gasoline varied substantially in each car. Variations were mostly a function of the amount of undersize collected on the absolute filter backing up the last stage of the impactor. This filter collects some adsorbed material from the exhaust and its weight is variable from test to test.

Total Particulate Mass Loadings

The exhaust particles collected from each car run through four modified LA-4 cycles on unleaded gasoline were weighed to determine mass emissions. The effects of different face velocities on the collected mass of particulates were investigated by making simultaneous collections on 47-mm and 142-mm diameter Metricel-DM filters and on a Battelle cascade impactor with a 76-mm Metricel backup filter. All sampling rates were 1 cfm.

The 1967 Chevrolet was also used in this series to compare collections from four modified LA-4 cycles with leaded and with unleaded gasolines. The results are presented in Table 9.

Later experiments compared the mass of particulates emitted during four hours at 50-mph steady-state from the blue car (leaded fuel RE-141C) and white car (unleaded fuel RE-141B). Again the effects of face velocity

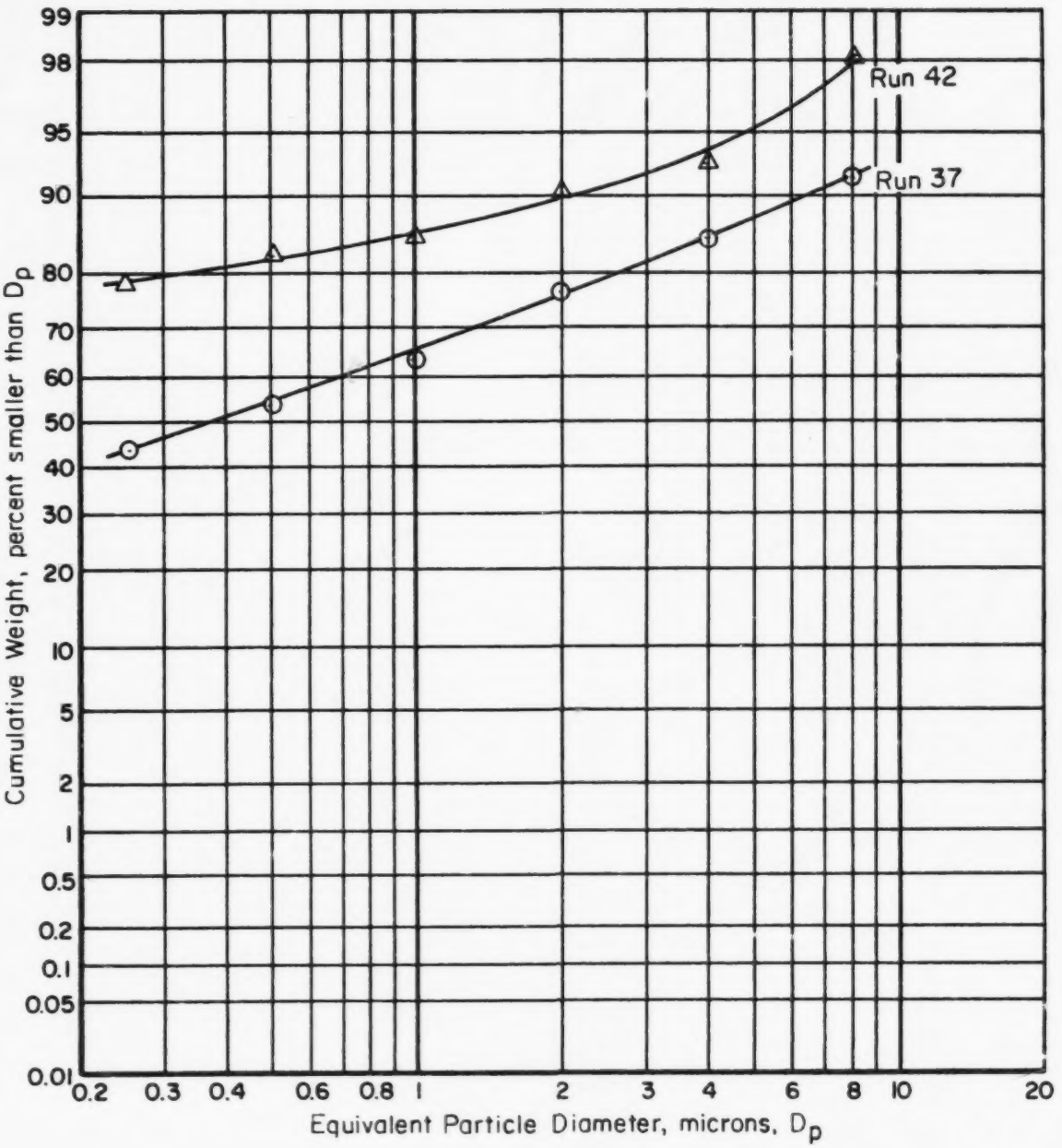


FIGURE 17. PARTICLE SIZE DISTRIBUTION IN AUTO EXHAUST GENERATED BY THE WHITE CAR WITH UNLEADED GASOLINE RE-141B

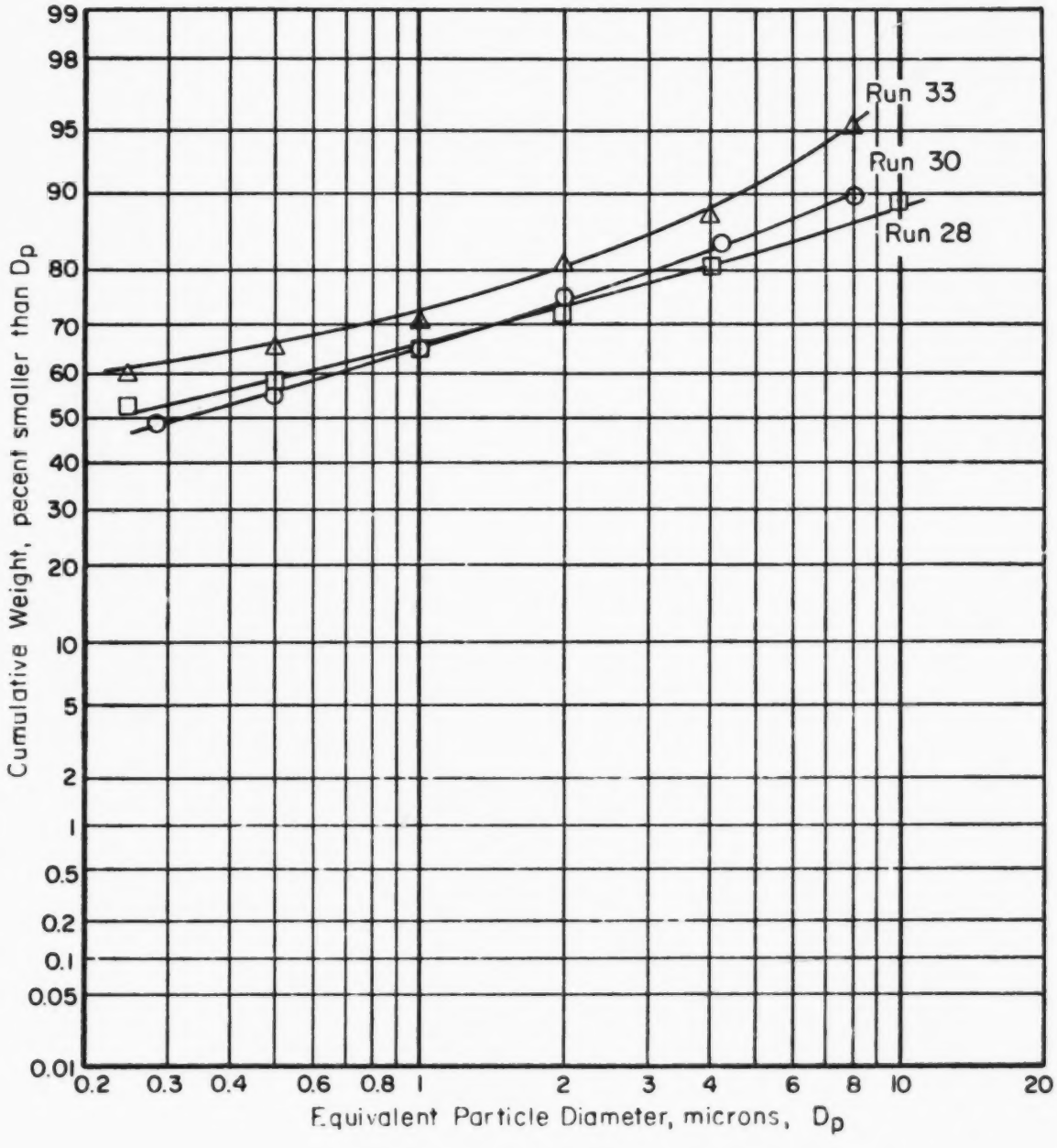


FIGURE 18. PARTICLE SIZE DISTRIBUTION IN AUTO EXHAUST GENERATED BY THE BLUE CAR WITH UNLEADED GASOLINE RL-1418

TABLE 9. COMBINED WEIGHTS OF AUTO EXHAUST PARTICULATES FROM UNLEADED FUELS FROM FOUR MODIFIED COLD-START[a] LA-4 CYCLES ON "METRICEL-DM" FILTERS AND ON THE CASCADE IMPACTOR WITH BACK-UP FILTER

Automobile	Mass of Particles Collected					
	47-mm Filter[e]		142-mm Filter[e]		Impactor and 76-mm Filter[e]	
	mg	g/mi	mg	g/mi	mg	g/mi
Blue Car, Unleaded fuel	0.362	0.007	1.209	0.024	-	-
Ditto	1.578	0.032	2.083	0.042	1.783	0.036
"	0.520	0.010	-(b)	-	0.566	0.011
"	0.444	0.009	0.805	0.016	0.441	0.009
"	0.638	0.013	1.100	0.022	0.805	0.016
Mean		.014±.011		.026±.013		.018±.013
White Car, Unleaded fuel	0.446	0.009	1.117	0.022	-	-
Ditto	0.556	0.011	0.750	0.015	0.960	0.019
"	0.423	0.008	0.740	0.015	0.663	0.013
"	0.327	0.007	0.995	0.020	-(c)	-
"	0.540	0.011	1.112	0.022	-(c)	-
" (d)	0.810	0.011	1.603	0.032	0.653	0.013
Mean		.010±.002		.023±.007		.015±.004
1967 Car, Unleaded fuel	1.130	0.023	3.255	0.069	1.052	0.022
1967 Car, Leaded fuel	1.0251	0.021	0.555	0.012	1.051	0.022

(a) Cold-start cycle after rapid cooldown.
(b) Filter holder came apart during test.
(c) Negative weight obtained on high velocity stage.
(d) Six LA-4 cycles were collected on stainless steel shim stock.
(e) Filter constants:

Dia., mm	47	142	76
Active area, cm^2	9.6	125	21.2
Face Velocity at 1 cfm, cm/s	49.2	3.8	22.3.

(f) Conversion factor: $\frac{mg}{1000} \times \frac{\text{total flow}}{\text{sample flow}} \times \frac{1}{\text{distance, mi}} = g/mi.$

Exhaust flow, 30 cfm; tunnel flow, 600 cfm; LA-4 cycle, 7.5 mi.

$\frac{1}{1000} \times \frac{600}{1} \times \frac{1}{4 \times 7.5} = 0.020$ [except footnote (d)]. Mean collection for two project cars: 47-mm filter, 0.58 mg or 0.012 g/mi; 142-mm filter, 1.10 mg or 0.023 g/mi.

were studied by collecting parallel samples on 47-mm and 142-mm-diameter filters and in the Battelle cascade impactor including the 76-mm back-up filter. The results are shown in Table 10.

Calculating from the effective filtration areas of the 47-mm and 142-mm-diameter filters, the ratio of the face velocities at 1 cfm total flow rate is about 13:1. Because the collection efficiency of both filters is extremely high, little difference in the total collections would be anticipated. Nevertheless, large differences were observed between the total mass of particulate collected by the two filter diameters. The 47-mm filter almost always collected less material than the 142-mm filter, under otherwise comparable conditions. This face velocity effect has been observed by others, but the mechanism is unknown.

In view of the difficulty of obtaining consistent collection of unleaded auto exhaust particulate at differing face velocities, comparisons of total mass loadings based on filter collections are arbitrarily made with samples taken at the lower face velocities by the 142-mm filter. Comparisons of total mass emissions on the 142-mm filter collections at 1 cfm from data in Tables 9 and 10 above indicate that the particulate mass loadings from the project cars are much lower at steady 50-mph cruise than with the modified LA-4 cycle. The absolut amounts of the particulates collected are much lower than the amounts reported by others with different cycles and different cars.[1] The lower amounts probably come from a combination of causes, including differences in cooldown procedure, carburetor idle, jet adjustment, and choke action.

---

(1) See review by K. Habibi, Environmental Science and Technology, Vol. 7, pp. 223-233 (1973).

TABLE 10. WEIGHT OF AUTO EXHAUST PARTICULATES COLLECTED ON METRICEL-DM FILTERS OF DIFFERENT SIZES AND ON CASCADE IMPACTOR

(4-hour samples at 50 mph steady-state)

Test No.	Project Car	Gasoline	Mass of Particulates Collected (b)					
			47-mm Filter		142-mm Filter		Cascade Impactor	
			mg	g/mi	mg	g/mi	mg	g/mi
43	White	Unleaded (RE-141B)	0.761	0.0015	0.965	0.0019	0.703	0.0014
47	White	Unleaded (RE-141B)	0.403	0.0008	0.241	0.0005	0.733	0.0015
		Mean		0.0012		0.0012		0.0015
48	Blue	Leaded (RE-141C)	3.082	0.006	(a)	-	3.495	0.007
50	Blue	Leaded (RE-141C)	4.095	0.008	7.295	0.015	3.771	0.008
		Mean		0.007		0.015		0.008

(a) Invalid because hose came off filter holder during test.

(b) Conversion factor: $\frac{\text{mg}}{1000} \times \frac{\text{total flow}}{\text{sample flow}} \times \frac{1}{\text{distance, mi}} = \text{g/mi}$

Sample flow, 1 cfm; exhaust flow, 54 cfm; tunnel flow, 400 cfm; distance, 200 mi.

$$\frac{1}{1000} \cdot \frac{400}{1} \cdot \frac{1}{200} = 0.0020.$$

To determine MMED data at 50 mph from the white unleaded car fueled with unleaded gasoline RE-141B, and from the blue leaded car fueled with leaded gasoline RE-141C, samples were taken for four consecutive hours. The results are plotted in Figures 19 and 20. Sixty-six weight percent of the leaded exhaust particulates were smaller than 0.25 μm whereas only approximately 35 weight-percent of the unleaded particulates were smaller than 0.25 μm.

When the white car was fueled with unleaded gasoline, there was a substantial difference between Runs 37 and 42 (Figure 17) in the proportionate amounts of small sized and undersize particles collected. However, there was good agreement over the whole size range from the blue car in Runs 28, 30, and 33 (Figure 18). Approximately 56 weight percent of the exhaust particles from unleaded fuel are below 0.25 μm.

Factors Affecting Light Scattering in the Tunnel

Consistency in running cold-start LA-4 cycles for particulate sampling is important, but a procedure which reproduces exhaust aerosol characteristics has been difficult to establish. Repeated measurements of light scatter in the dilution tunnel, mass emissions measurements, chemical composition, plus examination of shade and distribution of collected material on the filters revealed a lack of consistency in quantities and appearance even with the carefully duplicated rapid cooldown procedure. Therefore, the influence on exhaust aerosols of engine temperatures, cooldown time, and cold-start procedures was investigated briefly.

This investigation included variations in cooldown time, selective cooling, and controlling choke action. In connection with choke action, it

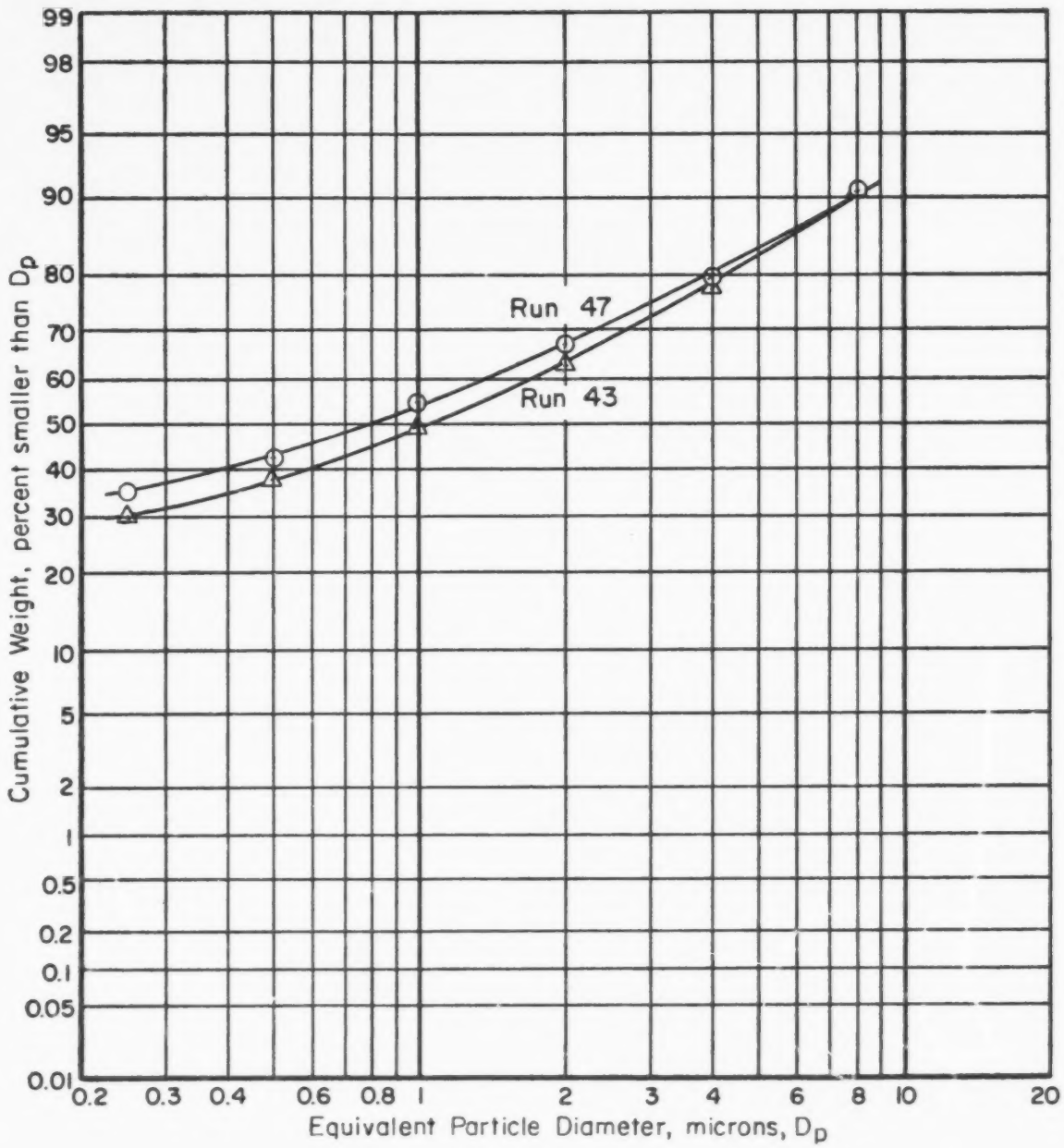


FIGURE 19. PARTICLE SIZE DISTRIBUTION IN AUTOMOBILE EXHAUST GENERATED BY THE WHITE CAR WITH UNLEADED GASOLINE AT 50 MPH STEADY STATE

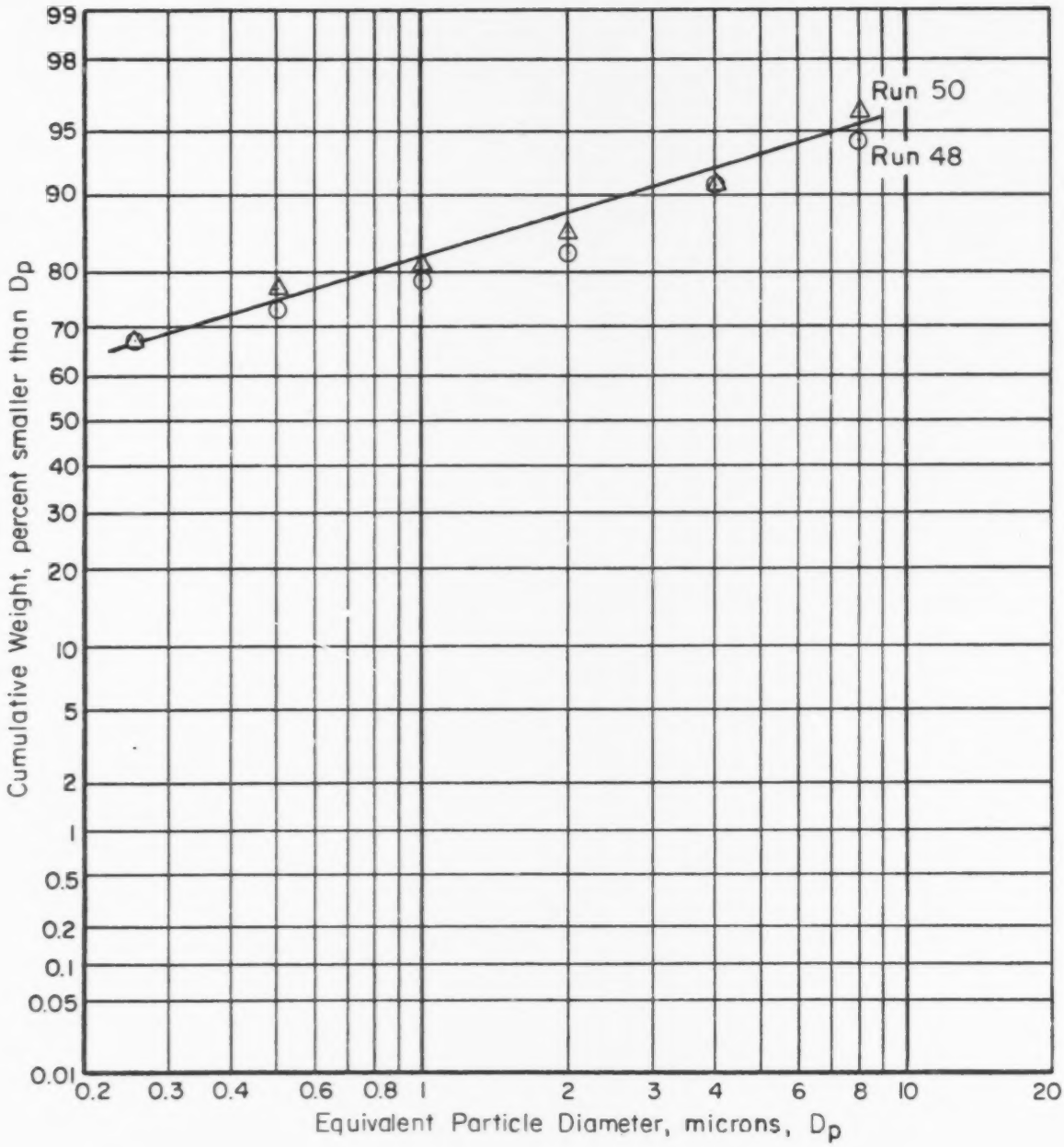


FIGURE 20. PARTICLE SIZE DISTRIBUTION IN AUTOMOBILE EXHAUST GENERATED BY THE BLUE CAR WITH LEADED GASOLINE AT 50 MPH STEADY STATE

had been decided with the CAPE-19 Project Group that controlled choke operation would be a part of the operating procedure. The blue leaded car operating on leaded fuel RE-141C was used in this study and the choke was modified during the course of the experiments.

A total of 24 modified LA-4 cycles were run with various conditions of cooldown with the unmodified choke. Variations included length of cooldown time (from three minutes to over-the-weekend), laboratory ambient temperature (70 F and 40-50 F), and selective cooling (cooling water, exhaust system, radiator, choke box, and oil pan). The tunnel was operated at 600 cfm to give an average dilution ratio of 20:1 in the tunnel for modified LA-4 cycles, which were run with the dynamometer preset at 12 HP load at 50 mph. At this setting, the modified LA-4 cycle generates exhaust gas at an average rate of 30 cfm. The Sinclair-Phoenix photometer was used to measure light scattering at the downstream end of the tunnel. The car was usually only operated through the first ten minutes of the cycle when most light-scattering effects are observed. The full cycle was run in a few experiments to establish the light-scattering pattern of the full cycle. Light-scattering effects were negligible after ten minutes of the cycle.

Figure 21 shows light-scattering curves recorded from three runs of widely different conditions. The first curve resulted from an overnight soak, the next curve from a 17-minute cooldown with all cooling on, and the last curve from a 12-minute cooldown. The influence of the different cooldown conditions is significant. These curves of Figure 21 are reasonably typical of all the data, although there were exceptions that did not follow quite as clear a trend of light-scattering versus cooldown time as illustrated. Each of these three curves shows distinct "bursts" of light scattering following the acceleration parts of the first five modes of the cycle.

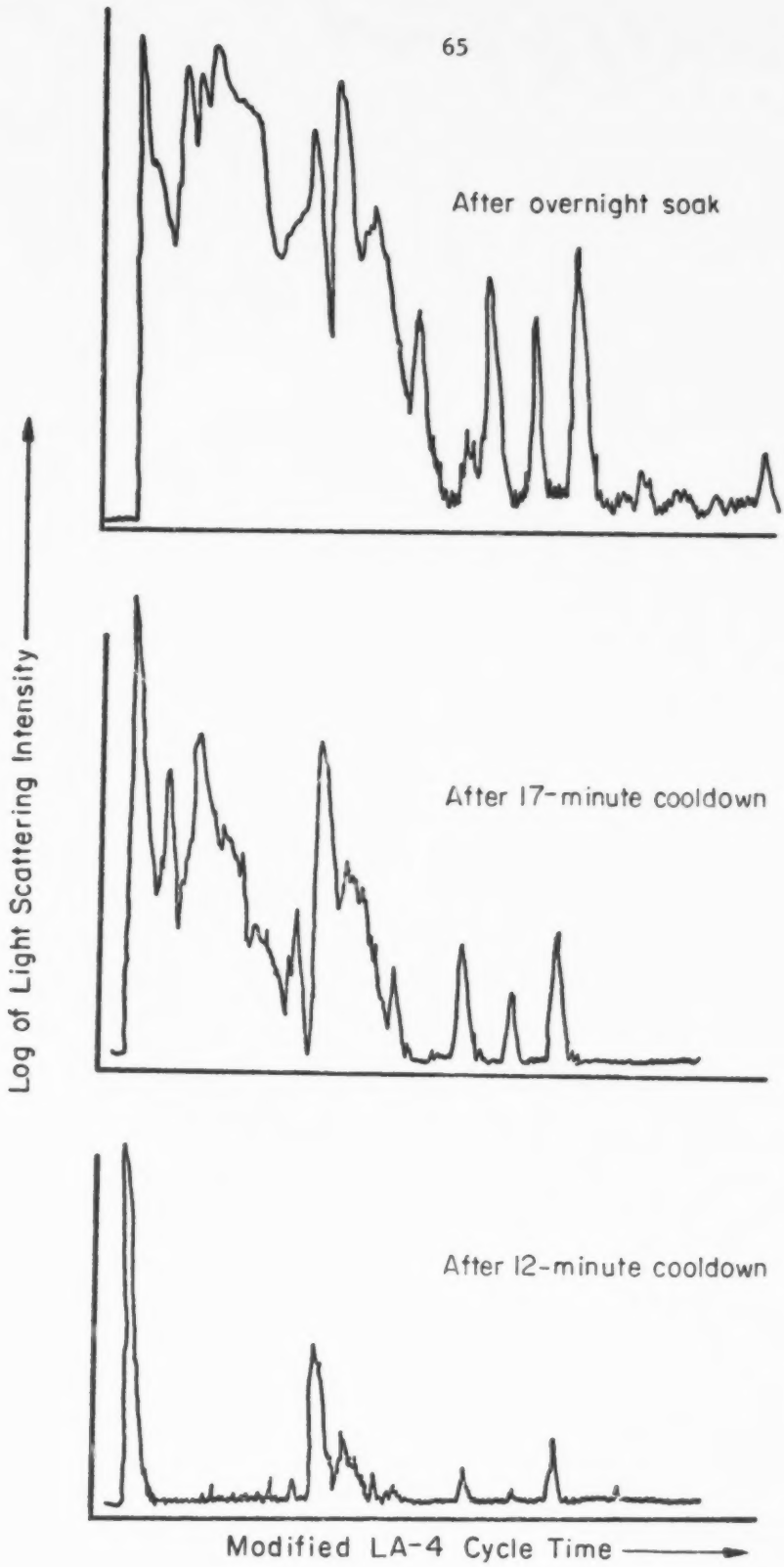


FIGURE 21. TYPICAL LIGHT-SCATTERING PATTERNS FOR DIFFERENT INITIAL TEMPERATURE CONDITIONS, BLUE CAR

Figure 22 shows the area under the light-scattering curves of all 24 test runs plotted against the choke box temperature at the start of the run. The lower the initial temperature, the greater the light scatter. At the choke-box temperatures in the range 40 to 60 F, light scattering was extremely sensitive to small changes in temperature, whereas, at higher choke-box temperatures, the effect is less. The light-scattering intensity is recorded on a log scale by the instrument and areas under the curves plotted in Figure 22 were measured without converting to a linear scale. Qualitative correlation between choke-box temperature and light scatter is evident.

After these tests, the choke was modified for controlled operation. The entire assembly containing the bi-metal coil spring was replaced by a shaft which could be rotated by hand to move the choke through its 60 degrees of arc from full closed to full open. A quadrant plate with 5-degree marks was mounted over the shaft to indicate choke position. A leaf spring connected the shaft with the slotted choke lever to permit the choke plate to be moved by the action of air flow into the carburetor.

Another 24 modified LA-4 cycle runs were made with manually controlled choke action. Most of these runs were made using a constant cooldown period of 12 minutes; in this period, all temperatures but the oil dropped below 100 F. Several different choke-opening schedules were tried for these test runs. The car started with difficulty and idled roughly if the choke was fully closed; hence, all runs were made with the choke initially at 5 degrees open.

Figure 23 shows light-scattering data for three consecutive 12-minute cold-start partial modified LA-4 cycles. The choke-opening schedule (Schedule 1) used for these test runs was as follows: start at 5 degrees open, move 10 degrees/minute to 55 degrees. Thus, the choke was

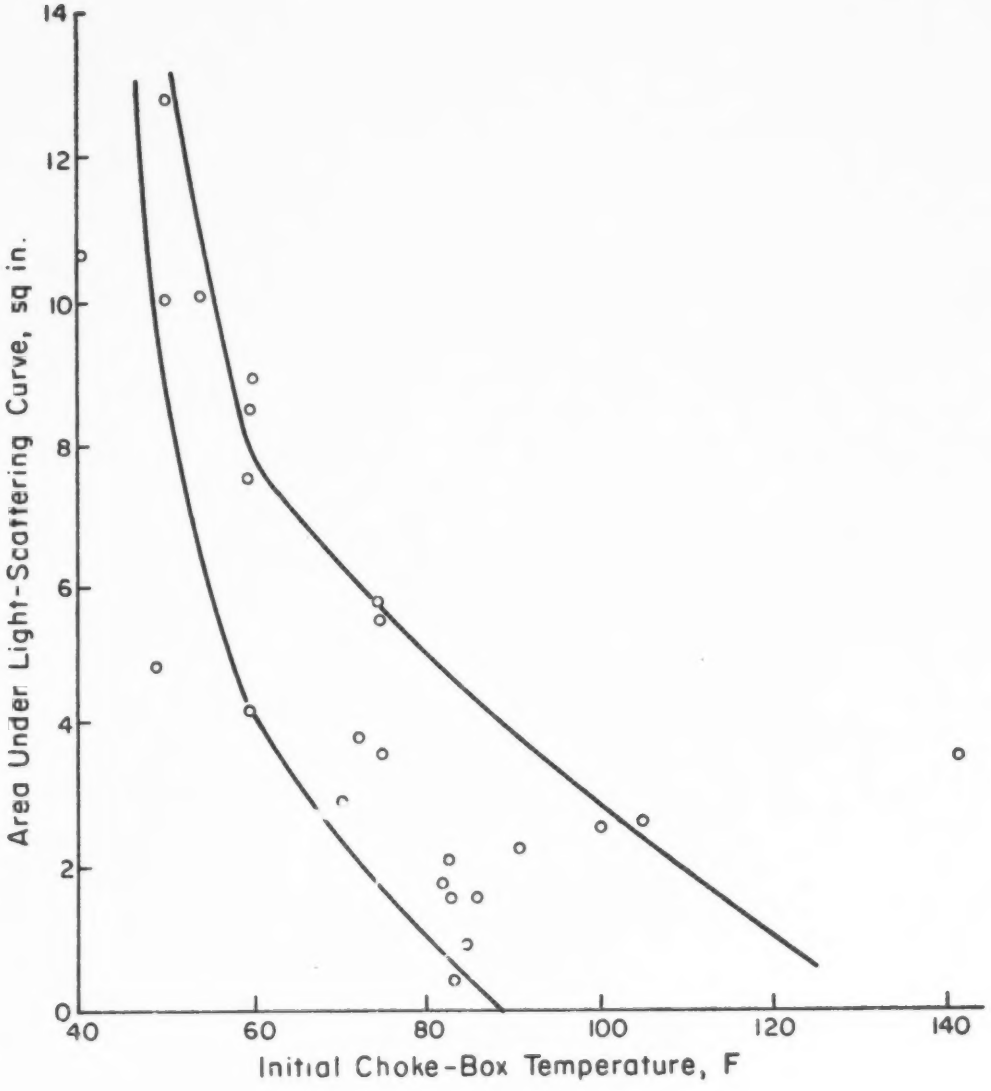


FIGURE 22. CORRELATION BETWEEN LIGHT-SCATTERING AND INITIAL CHOKE-BOX TEMPERATURE, BLUE FORD

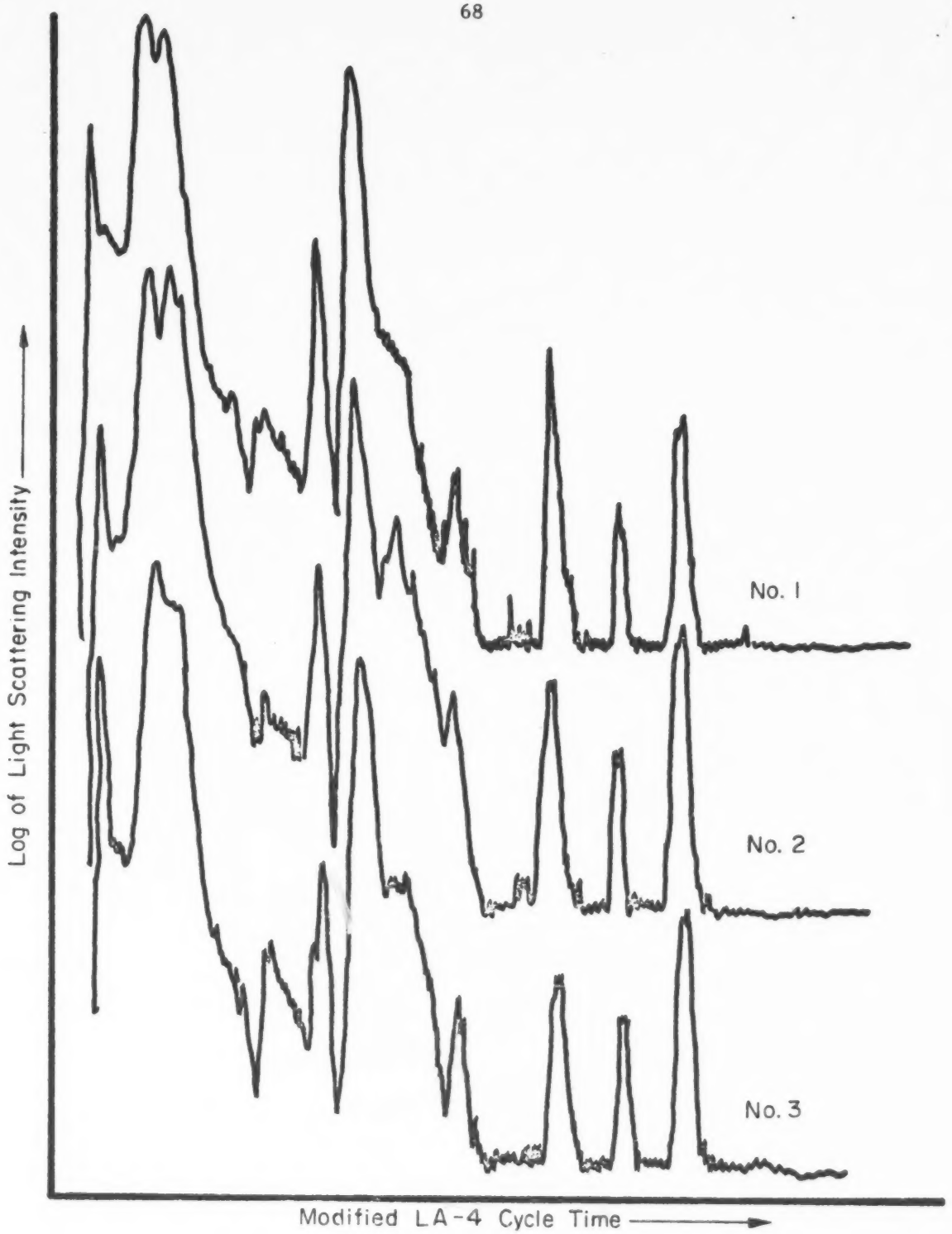


FIGURE 23. LIGHT-SCATTERING PATTERNS FOR CONSECUTIVE PARTIAL MODIFIED LA-4 CYCLES USING CONTROLLED-CHOKE SCHEDULE 2 - BLUE CAR

almost fully open in 5 minutes. The light scattering is moderate and consistent.

Figure 24 shows light-scatterin, data for another series of three more similar cold-start modified LA-4 cycles. The choke-opening schedule (Schedule 2) used for these test runs was as follows: start at 5 degrees open, move 5 degrees/minute to 20 degrees, move 20 degrees/minute to 60 degrees. The fully open position is again reached in 5 minutes, but more choking takes place in the first 3 minutes than for the runs illustrated in Figure 24. The light-scattering intensity is greater because of the increased choking but the cycles are still quite consistent.

This investigation demonstrated that choke control gives acceptable light-scattering reproducibility in repeated test runs.

Preliminary Residence Chamber Measurements

Test Conditions

After three exploratory tests in which no particles were collected from the residence chamber, Run 4 gave preliminary data on the particle content of the chamber. The sample line was installed and the tunnel sample-point pressure selected before the sample flow into the chamber could be measured. Sample flow was greater than anticipated, so that the final dilution in the chamber was about 150:1. Although this was not the target dilution ratio of 300:1, the results from the following experiment were useful in evaluating systems performance and feasibility.

Instruments used during Run 4 described below were: Sinclair-Phoenix Photometer, Integrating Nephelometer, Particle Mass Monitor, Condensation Nuclei Monitor, and Single Particle Counter. In addition, particulate

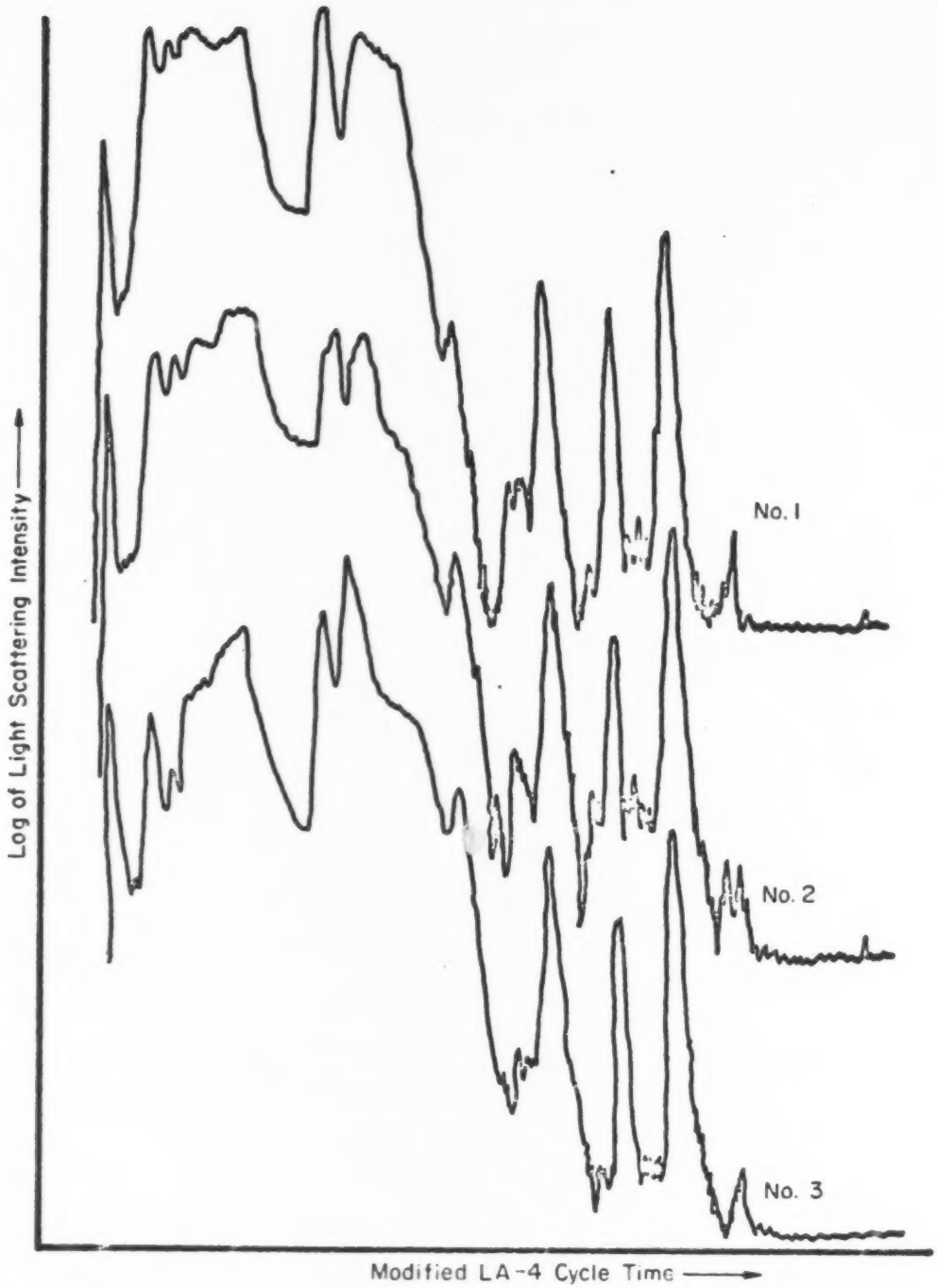


FIGURE 24. LIGHT-SCATTERING PATTERNS FOR CONSECUTIVE PARTIAL MODIFIED LA-4 CYCLES USING CONTROLLED-CHOKE SCHEDULE 2 - BLUE CAR

samples were collected from the chamber using 142-mm and 47-mm filters and the Battelle cascade impactor.

During the chamber run, data were recorded periodically, beginning before the start of the cycle and up to 6-1/2 hours of residence time. Additional data were recorded the next day up to 24 hours of residence time.

Aerosol Concentrations

The white project car was operated on unleaded fuel RE-141B for one modified LA-4 cycle to generate exhaust particles in the tunnel for sampling into the residence chamber.

Figure 25 shows graphically the results from the Integrating Nephelometer, Particle Mass Monitor, and Condensation Nuclei Monitor for the first 6-1/2 hours of residence time, plotted as a percentage of the maximum values recorded. Measurements at 21 to 24 hours of condensation nuclei count and of light scatter by the integrating nephalometer showed no further change from the readings at 6-1/2 hours. The particle Mass Monitor did not seem to be working properly at 24 hours residence time.

Light scatter by the Sinclair-Phoenix Photometer (not shown) were very similar to data from the Integrating Nephelometer, with a peak value reached at 1.6 hours and no further change at 24 hours.

Particle Count

In some experiments, light scatter was also measured with a Single Particle Counter. The instrument has a lower size limit of about 0.3 μm, and light scatter from particles in the range 0.3 to 4.0 μm is

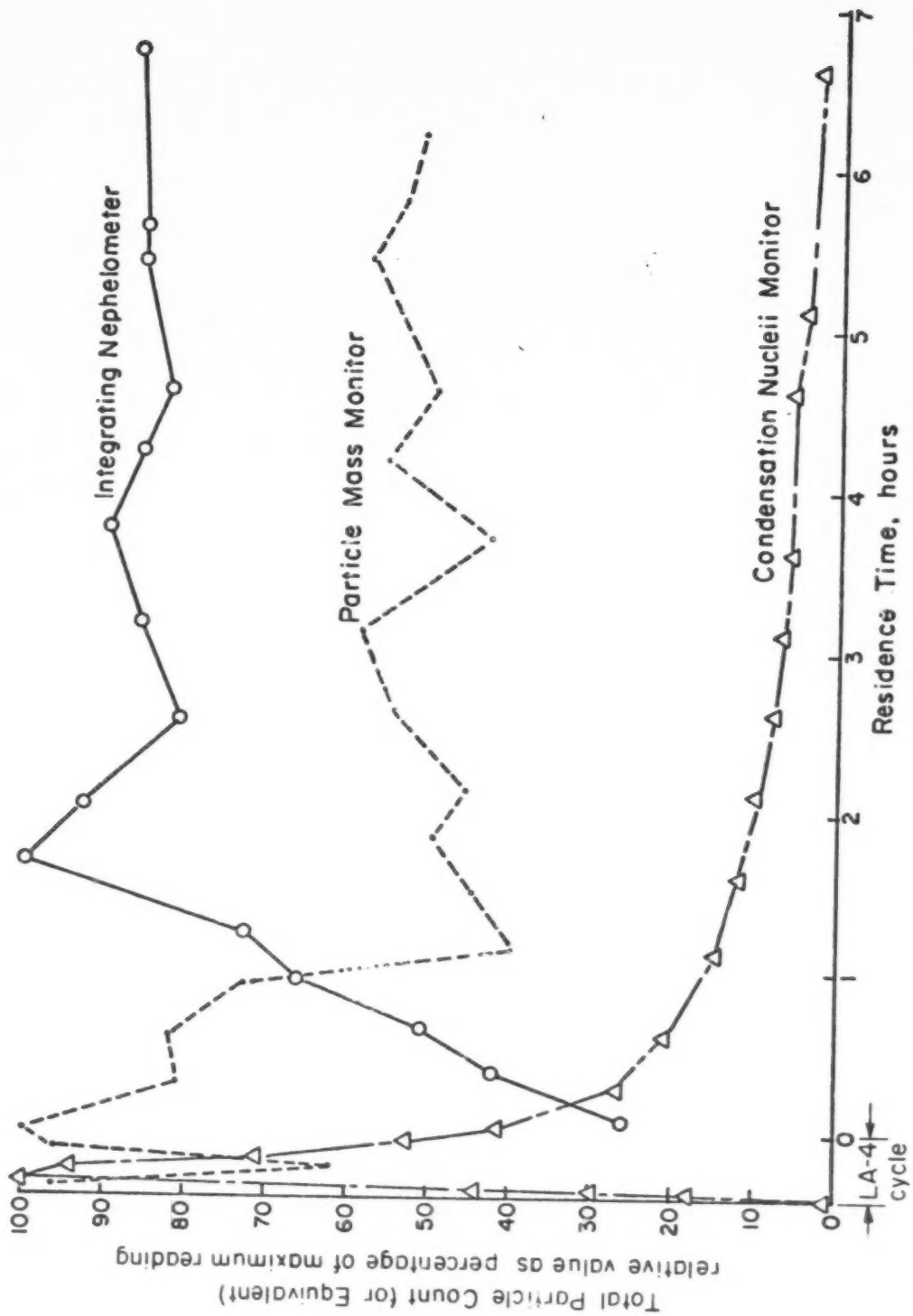


FIGURE 25. PARTICLES IN RESIDENCE CHAMBER, RUN 4
(White car with unleaded fuel RE-141B for one modified LA-4 cycle at a dilution of 150:1)

measured in 256 size classes. A particle count can be made over any time period; however, the dilute aerosol in these experiments requires 10 minutes to obtain an adequate size distribution. The data were presented on an oscilloscope as the counts accumulated and at the completion of the (10-minute) count the totals were recorded numerically. These data are described qualitatively below but are not shown in detail because Run No. 4 was exploratory.

The total particles counted by the Single Particle Counter came to a constant count at about two hours. However, in the smaller size range of the classifications of the Particle Counter (not shown), there was initially a slight decrease and then a continual increase for the next 24 hours of the test. Conversely, there was a noticeable decrease in the number of particles in the larger range (2-4 μm) during the whole 24-hour period. This pattern indicates that the smallest particles below the counting range were growing by agglomeration to a detectable size and the largest particles were precipitating out of the aerosol.

Particle Mass

Three concurrent 60-minute samples were taken after four hours residence (R = 4 hr) in the chamber, each at a rate of 1.0 cfm, using the Battelle cascade impactor and two different sizes of absolute filters. (The 60-minute samples were taken from R-30 minutes to R+30 minutes.) Figure 26 is a plot of the data from the cascade impactor. The curve shows that 73 percent of the mass was less than 0.25 micron. The weight found at each of the six impactor stages varied between 17 and 25 micrograms, and there were 363 μg on the 76-mm backup filter. A total of 497 micrograms was

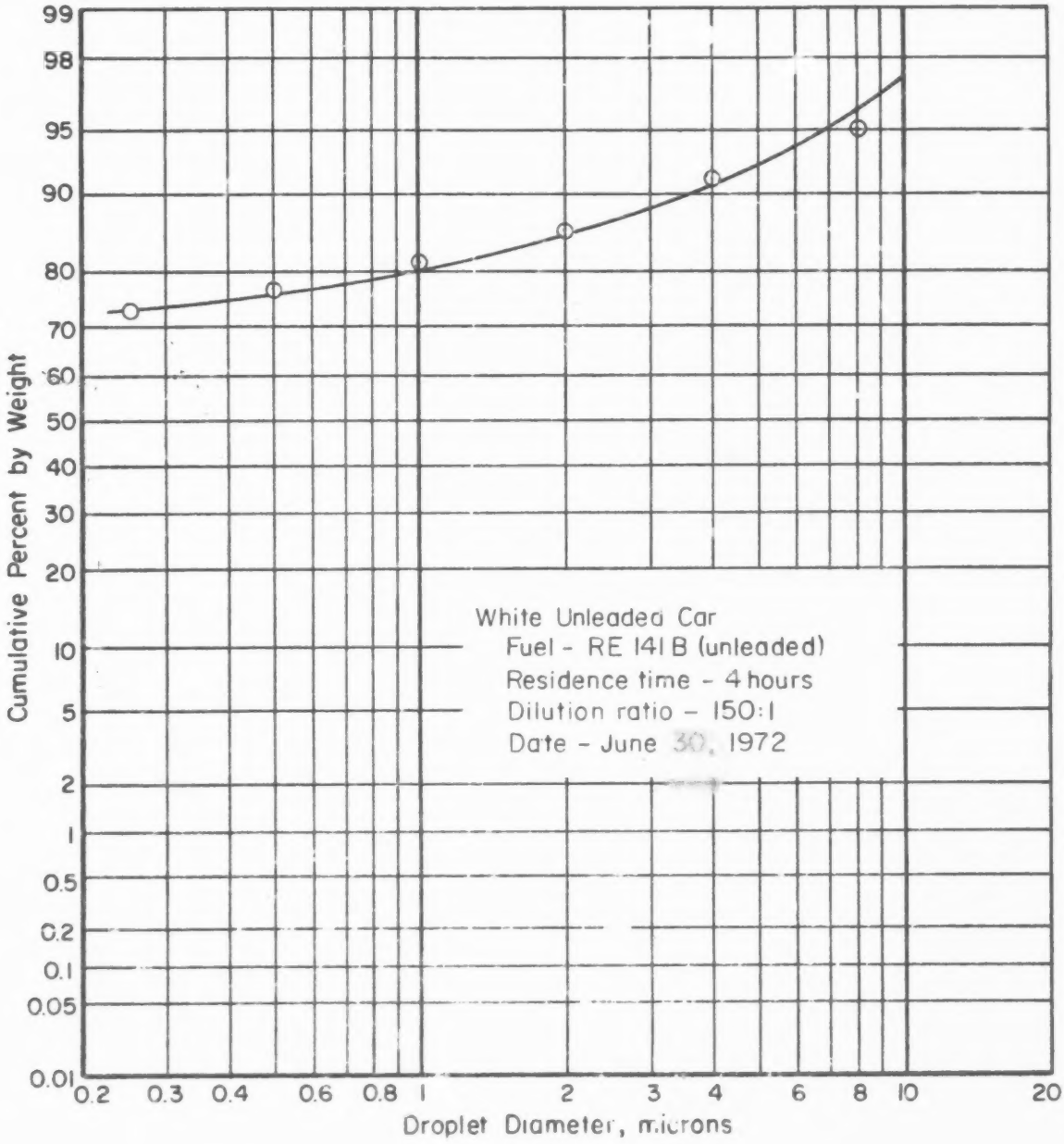
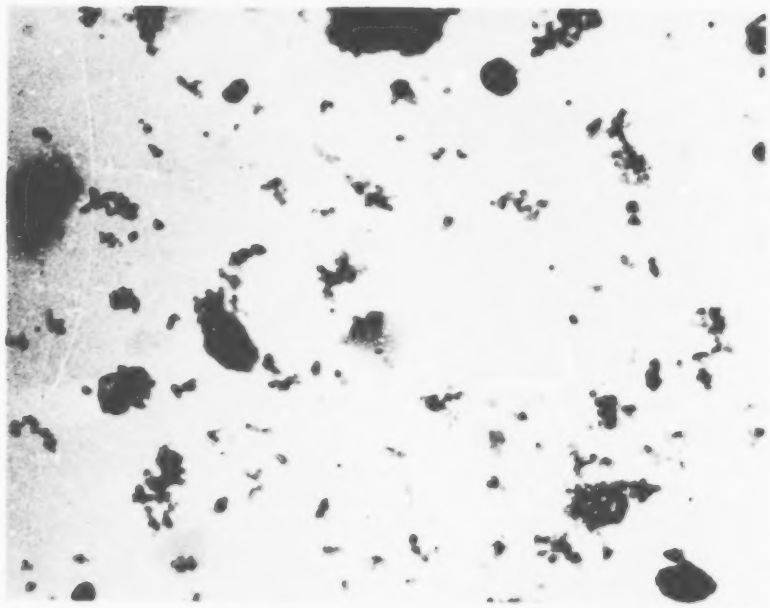


FIGURE 26. PARTICLE SIZE DISTRIBUTION OF DILUTED AUTOMOBILE EXHAUST IN CHAMBER (Run 4)

collected by the impactor. The 142-mm absolute filter collected 705 micrograms, whereas the 47-mm-diameter absolute filter collected 96 micrograms. Because of these wide variations of 96, 497, and 705 μg in amounts collected, additional runs must be made with duplicate samples to examine the source of the variations.

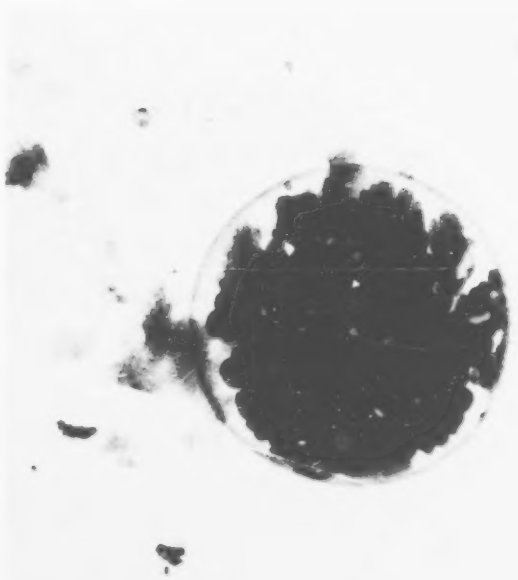
Particle Morphology

Particle morphology was determined by transmission electron microscopy performed on collections made after six hours residence. Almost all particles collected were under 1.0 μm. The most prevalent particle found at the 0.25 μm stage was carbon black (Figure 27). The particle type most prevalent in the 0.5 and 1.0 μm size ranges was the droplet structure containing crystal growths appearing to have been nucleated by a small particle (Figure 28). Both the carbon black and droplet-type particle found in the residence chamber have been found previously in exhaust from unleaded gasoline in the dilution tunnel (Figures 15 and 16).



J20956 20,000X

FIGURE 27. PARTICLES COLLECTED ON THE 1/4-μm IMPACTOR STAGE AFTER SIX HOURS IN THE RESIDENCE CHAMBER



J20950 20,000X

FIGURE 28. A PARTICLE TYPICAL OF THOSE COLLECTED ON THE 1.0-μm IMPACTOR STAGE AFTER SIX HOURS RESIDENCE TIME

MAJOR ACCOMPLISHMENTS

1. Standardization of Test Autos

Two matched autos have been made operative to generate exhaust particulate matter. These 1970 Fords are equipped with measured and matched 1971 351 CID engines Model 351C, automatic transmissions, and 2-barrel carburetors. The autos are as nearly identical as possible except for color, which identifies the white car as using only unleaded gasoline, and the blue car only leaded gasoline following a break-in on unleaded gasoline. These cars were chosen to represent a typical and large-volume sales U.S.A. car model. To achieve reproducible operation of the cars for generating the exhaust particles, they are driven under consistent dynamometer load conditions in the laboratory, using an automatic driving system, controlled by a tape, to repeat precisely the selected driving cycle in each test run. The cars are instrumented with thermocouples at strategic positions to show that temperatures are normal during conditioning before each test, after an overnight wait for the car to cool to a reproducible initial state, and during operation in the test run. Forced air cooling is used during the tests to maintain operating temperatures at levels closely similar to measured values during operation on the highway.

A typical unleaded fuel was purchased in sufficient quantity to supply the projected needs of the project to its completion, and this fuel was also used for preparing leaded fuel. Thus, both fuels have identical compositions except for added lead compound and scavenger in the leaded fuel.

2. Construction and Operation of Test Facility

As the exhaust issues from the tailpipe, the particles are quenched and diluted with atmospheric air to simulate release into the free atmosphere. A dilution tunnel has been built and calibrated to receive the exhaust into a controlled flow of filtered air. The exhaust and air pass through a measuring and mixing orifice and along the length of the 36-foot stainless steel tunnel past sampling ports at 6-foot intervals. Typically, the exhaust is diluted 20:1 or 30:1 by appropriate control of the tunnel air flow.

Instrumentation was assembled and is in use to monitor exhaust gas composition continuously for CO, HC, CO_2, and NO in the tunnel in order to appraise reproducibility of operation. A composite sample of gas from the tunnel is withdrawn into a storage bag during cyclic operation of the car for analysis to determine average composition of exhaust during variable modes of operation.

A residence chamber has been constructed and used to isolate a composite sample of the tunnel flow diluted further ten-fold to a final dilution of about 300:1 for the exhaust. A volume of 2100 cu ft of the final dilution is collected and can be held in the chamber for extended periods. The gas is sampled periodically to examine composition, particle content, and light-scattering properties for evidence of the physical and chemical characteristics of exhaust particles as a function of their exposure time in the atmosphere. Walls of the chamber are flexible, opaque film mounted on a collapsible frame to minimize photochemical interactions, and to maintain negligible pressure difference between sample and surroundings while the chamber is in use to collect, store, and then withdraw samples

of diluted exhaust. Instrumentation is extensive for measuring and recording temperature, humidity, gaseous composition, and particle content by various procedures.

3. Conditioning of Cars

Each of the two cars has been conditioned for deposit stabilization for a total of about 9000 miles. Initially, each car was driven for 4000 miles with unleaded fuel on a (modified) Durability Driving Schedule. Periodic tests during the stabilization run and after 4000 miles established their matched condition. Stabilization was completed after operation for another 4000 miles on the Durability Driving Schedule with unleaded fuel in one car and leaded fuel in the other. Samples are generated for examination of exhaust particles by the modified LA-4 cycle from a cold start or from operation at 50 mph cruise mode.

4. Preliminary Particulate Measurements

Experimental measurements of the mass of particulate emissions collected on Metricel-DM 450 membrane filters showed variations in the collected amounts with the face velocity of the diluted exhaust approaching the filter, as well as with the operating cycle and fuel used. Mean values of particulate emissions from the matched cars during modified LA-4 cycles using unleaded fuel were 0.010 ± 0.002 (white) and 0.014 ± 0.011 (blue) g/mi on the 47-mm filter, and 0.023 ± 0.007 (white) and 0.026 ± 0.013 (blue) g/mi on the 142-mm filters. Comparable collections on 47-mm filters during 50 mph cruise were 0.0012 g/mile from unleaded fuel in the white car, and 0.007 g/mile from leaded fuel in the blue car.

Particle-size distributions of particles were measured in the Battelle impactor, which collects fractions on six impact stages with cut-offs at sizes ranging from 8 to 0.25 micrometers mass mean equivalent diameter. The undersize particles are collected on an absolute filter backing up the last stage with a mean pore diameter of 0.45 μm. Weights collected from four consecutive cold-start modified LA-4 cycles in each of five experimental runs showed a predominance of undersize from unleaded fuel with a mean of 56 percent of the total weight on the backup filter

The morphology of particles from the dilution tunnel with each car operating on unleaded fuel was examined and compared to determine the similarity of the matched cars. Two types of particles predominated in the samples. Particles on the 0.25 micrometer stage appeared similar to carbon black, and particles on the 0.5 micrometer stage resembled tar droplets with a spherical envelope surrounding a crystalline core.

The chemical nature of the particles was examined for both inorganic and organic constituents to measure metals content of the exhaust particles and to search for detectable amounts of polynuclear aromatic hydrocarbons or other significant organic components. The amounts of samples that could be collected were so small from the diluted aerosol from unleaded gasoline exhaust that metals detected were not significantly above background levels in the filtered dilution air. No single organic compounds nor significant classes of compounds could be identified in the extract from the small quantity of exhaust particulate available by the chromatographic methods used.

The properties of the aerosol particles in diluted exhaust were examined in exploratory measurements while the aerosol was aged in the residence chamber. The number of condensation nuclei decreased steadily after the chamber was charged and dilution mixing was completed. Conversely, the light-scattering properties of the aerosol, as measured by the integrating nephelometer, increased markedly in the first 1.6 hours of aging, decreased between 1.6 and 2.5 hours, and then remained approximately constant. The overall results in these preliminary studies suggest that the smallest particles below the light-scattering range agglomerate or grow during the first two hours to a size sufficient to scatter light. Thereafter, light-scattering measurements indicate little change in the aerosol. Other measurements by a single-particle counter, which classifies the counts into separate size ranges, indicate growth and agglomeration, with increasing numbers in the sizes detectable by this instrument. Some particle growth appears to continue as long as 24 hours, accompanied by precipitation of the largest particles, as the count decreases in the larger size classes.

Samples were withdrawn from the chamber after six hours residence and passed through 142-mm and 47-mm filters, and an impactor with backup 76-mm filter. The weight gains recorded after filtration of identical volumes of gas in concurrent samples (60 minutes at 1 cfm) varied widely and correlated positively with the diameters or areas of filters used. No conclusions were possible concerning the absolute weight concentration of the filterable aerosol particles.

Morphology of the particles collected in an impactor after six hours aging in the residence chamber was examined. They were similar to particles collected in earlier runs from the dilution tunnel.

FUTURE WORK

The studies on characterization of auto exhaust particles will be continued with the use of the residence chamber for holding a diluted portion of the generated auto exhaust to examine the aerosol for changes in properties of the particles in the dark. The changes attributable to leaded vs. unleaded fuel, residence time, relative humidity, and the concentrations of two common atmospheric pollutants will be studied in a series of tests designed to show statistically significant differences in particle properties.

The variability of weights of particles collected on filters resulting from variations in filter properties and in collection conditions represents a serious handicap in the search for quantitative interpretations of the characteristics of exhaust particulate matter in the atmosphere. Studies will be continued with comparison of results on a relative scale, and efforts to resolve the problem of measuring the absolute mass concentration of auto exhaust particulates will be continued.